Philipp Katzenstein

Bachelor in Chemical and Biochemical Engineering

Distillation Resistance: A quick cost and duty estimation for a simple distillation columns train

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Mentor: Prof. Dr. J. P. Lange, University of Twente/Shell

Adviser: Prof. Dr. S. R. A. Kersten, University of Twente

Co-Adviser: Dr. Ir. A. G. J. Van der Ham, University of Twente

Prof. Pedro Miguel Calado Simões, NOVA University of Lisbon

Comittee:

Chair: Mário Eusébio, Auxiliar Professor, NOVA University of Lisbon

Arguente(s): Pedro Simões, Auxiliar Professor, NOVA University of Lisbon

Member: Isabel Esteves, Auxiliar Professor, NOVA University of Lisbon

FACULDADE DE CIÊNCIAS E TECNOLOGIA
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Distillation Resistance: A quick cost and duty estimation for a simple distillation columns train

Abstract

Quick cost estimations for new processes, with no precedent working plants, in order to check their feasibility are very difficult to perform.

Duty requirements are needed to perform the cost estimations to check its profitability. Obtaining these energy needs for a process, or a specific section, are very time consuming and result in long periods of time before a conclusion can be made upon the viability of a process.

The distillation resistance could solve this problem by presenting a short cut to a quick duty estimation. This correlation is set out to preview the duty for a separation train consisting of simple distillation columns. Demonstrating the reliability of this correlation could in a very early stage of a project allow for a good indication on its feasibility of this section. Giving guidance based on its reaction and separation choice.

The main focus of this project is to validate this correlation by using a different information source than the one used for its elaboration. After some needed corrections for high H_{vap} associated compounds separations, a trustworthy validation of the proposed correlation is presented, giving in this way good signs for an overcome of the time needed to perform a valid duty estimation quickly.

In extension to the validation, an introduction for a similar duty estimation for the reaction section is shown, opening the door to a quick full process estimation in a near future. More research regarding heat exchanger contribution without knowing the flowsheet could make this reaction section model as assertive as the distillation section one prior is.

Finalizing the duty estimation with a correlated cost estimation, the outcome showed similar results to previous works from Jean Paul Lange [1]. Showing good estimation results within boundaries of -50% up to +100%. of the equation.

Keywords: Cost Estimation – Duty Estimation – Reaction Estimation-Distillation Columns

Resumo

Estimar custos de um processo de forma rápida para poder testar a viabilidade do mesmo é um processo árduo e comprido.

Mais tecnicamente, as necessidades de calor são fundamentais para analisar o projeto em termos de probabilidade de sucesso. Obter estas mesmas para um processo, ou para uma secção especifica do mesmo, demora muito tempo. Desta forma, atrasando a conclusão que possa ser retirada em relação a rentabilidade do processo.

A resistência da destilação aqui apresentada poderá resolver este problema ao permitir uma rápida estimação de calores. Esta correlação prevê a energia necessária para uma disposição de colunas de destilação simples em série. Validar esta correlação permite tirar conclusões em relação a sua viabilidade, em um momento bastante cedo do projeto. Esta mesma estimação apresentada pode de seguida permitir uma resposta em relação a reação e método de separação escolhidas, de forma a poder otimiza-los.

O foco principal deste projeto é a validação da correlação proposta utilizando uma fonte de dados diferente da utilizada para elaborar a mesma. Uma correção necessária correspondente a compostos que apresentavam altos valores de entalpias de vaporização (H_{vap}) teve que ser feita, permitindo a validação da equação. Com estes resultados um bom ponto de partida é dado respetivamente a uma futura rápida estimação de calores para um processo.

Adicionalmente a esta verificação, um inicio para uma estimação de calores similar, focada na secção da reação, é apresentado, abrindo o caminho para uma futura rápida estimação de calores para todo um processo. Mais investigação em relação aos permutadores de calor poderia tornar esta secção mais exata nos seus resultados.

Para finalizar correlacionando os calores obtidos e usando uma equação de estimação de custos, os resultados demonstraram serem similares a trabalhos anteriores de Jean Paul Lange[1]. Desta forma pode-se também verificar que dentro de um certo limite desta equação de -50% a +100% os custos fixos de uma secção podem ser estimados velozmente.

Palavras-chave: Estimação de custos – Processos de separação - Bio refinaria – Colunas de Destilação

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Glossary

CapEx – Capital Expenses

CEPCI – Chemical Engineering Plant Cost Index

Ω_{feed} – Distillation Resistance feed

Ω_{prod} - Distillation Resistance product

PPD – Process Plant Design

ISBL – Inside Battery Limits

IRR – Internal Return Rate

MHHE – McGraw High Hiller Education

NBP – Normal Boiling Point

NPV – Net Present Value

OSBL – Outside Battery Limits

OpEx – Operating Expenses

ΔT_{AB} – Boiling Point difference between compound A and B

1 Introduction

1.1 Current common cost estimation

Having as a scope of the research the preliminary CapEx estimation, a short introduction into the subject of cost estimation is needed.

Cost estimation has helped chemical engineers for at least 70 years to approximate eventual costs for a plant in order to prevent non-productive constructions, to test new technologies or new projects. With these estimations operating and capital costs can be approximated and with that a profit forecast can be reached.

The costs for a plant can be separated in 3 categories: fixed capital costs, the working capital and the production costs (variable and fixed).

For this research the main focus was on the variable production costs (duties) and also a part of the fixed capital cost. Investment, (ISBL) represented as CapEx.

The variable production costs, that represent the vast majority of the total production costs, are mainly determined by the feedstock charges. For this reasons the gross margins (revenue-raw materials) are usually used to estimate the operating margin.

The fixed capital cost can be sub-divided into 4 divisions: inside battery limits, frequently shortened to ISBL that represents the costs of the plant itself; the offsite battery limits, often called OSBL, representing the modifications and improvements needed at the site to build the plant, as well as utility centrals; engineering costs representing the costs associated to the designing, super visioning and similar during the project first steps and finally the contingency costs which are extra costs added to the budget to allow the prevention of variations from the initial cost estimation.

Although there are some quick and crude correlations available, usually to estimate a process as a whole a lot of time is needed. The fastest and easiest is to use historic data to get an estimate for a new plant, only condition: having a plant using the same technology and knowing its output rate. If the data is available the following equation can be used [2].

$$C_2 = C_1\left(\frac{S_1}{S_2}\right)^n \quad (1)$$

Where,

C_2 = ISBL capital cost of the plant with capacity S_2

C_1 = ISBL capital cost of the plant with capacity S_1

n = 0.6 (constant, average across the whole chemical industry)

Even tough, this method is extremely quick, for the majority of cases there is not enough information to use it. Normally for the lack of plants working with the same technology in industrial scale or because

it is a new technology. For this reason, this method cannot be applied a lot of times and as said if a new process is to be tested for its feasibility this correlation becomes useless.

A more common approach consists first of an intensive research of: the market conditions as well as the existent technologies.

Typically, this first part can take up to several months to get enough of the required data.

Having all the information available and knowing the size demanded to supply the market the real plant design can start.

In this second part equipment and utilities are defined using programs like *Aspen Plus*, *Unisim* or similar. For this calculations a lot of variables have to be taken into consideration as for example changes in pressure or temperature along the process as well as the materials for specific compounds and their specifications, needing to elaborate all this for each equipment in the whole process.

Next step with knowledge of the duties involved and conditions required for each equipment, duty-cost correlation or websites like Matche, MHHE can be used to obtain the monetary costs for the plant.

Finally having all costs gathered together and compared with the generated revenue, predictions can be made upon the affordability of the process, using parameters like IRR, NPV and others to make a decision if the project should be executed or not.

Important to point out is that in this classical approach the project is evaluated at a global basis, the technologies tested usually are from patents that englobe a lot of times a total flowsheet and with that also every equipment has already in some way been decided.

For this reason, it is very difficult, especially quickly, to identify difficulties in specific sections of a process that could be improved. Furthermore, in particular new processes can't be analysed quickly for feasibility, since the duty need requirements take a lot of time as seen before.

With the goal in mind to find a quicker way to have a valuable cost estimation, the research focuses on validating a faster way to arrive at the duty requirements for a process to decrease the working time associated to obtain results.

Here is where the distillation resistance comes into play. This correlation was developed to provide a quick duty estimation for a vital part of a process, the separation.

The concept was developed from fossil fuel plants and extended to biorefineries, a quickly growing industry sector pointed at the future, reducing dependence on oil and gas needs.

The highest interest until now for the biorefinery process had been the reaction section, where usually the focus is on conversion, selectivity and reactor conditions.

The separation section where: reactants that did not react, products and sub-products are separated to be: recycled, sent to waste or sold, are still vital for the viability of the process[3]. These separations can be made using various methods like extraction, distillation, adsorption, among others. Being the most

applied in the refinery and the most traditional the correlation focuses on the distillation process made up of simple distillation column trains.

The thought is to separate the compounds only based on their boiling points, which means this requires ideality of the mixture seen that for example the presence of azeotropes will change the separation condition.

In the case of the distillation resistance tested by Jean Paul Lange the main focus goes towards typical biorefinery issues in distillation columns: the instability of products at high temperatures or high dilution (in water) of the product streams. Destroying your product is never an option and distilling high amounts of water should only be applied in last case to avoid the high energy demand to vaporize the water.

The results obtained from this correlation are used in a first step to analyze if a separation using the distillation columns is doable, if not why is it not and which is the separation in the train generating all (or the majority) of the difficulties.

In a further analysis the distillation resistance can also, in some extend, be used to give an indication of the possible costs associated to separation section using known duty – CapEx correlations.

In this research the correlation was not tested specifically for biorefniery cases, for this reason this introduction to the subject is loomed in a broader context than just the biorefinery.

Resuming what has been said, as seen in the prior text cost estimations are usually time consuming, having as exception the rarer quick historical data estimation, which can not be applied to new processes. Downside beside the fact of lack of information's for similar process is also that a process is analysed as a total. This makes sense if a certain known technology as a whole is to be tested for profitability, on a new location for example. On other hand, if the designer would like to have a quick look at a certain part of a process to know its viability quickly or of a never used new technology for example, usually there is no way around than the long track, typical duty estimation, to get an estimate. The validation of the distillation resistance concept could solve part of this "problem", by enabling a short cut for the duty estimation. Overlooking the correlation, the idea is as followed.

Time consuming accessible data/long calculations (*Aspen*,*Unisim*) → **Duty** → Cost

↓ With the distillation resistance

Easy accessible data/quick calculations → **Duty** → Cost

1.2 Distillation Resistance Ω_{feed} - Development

In order to arrive at the distillation resistance correlation a closer look was taken at its origin: cost equations. Looking back, beside the more common estimations shown in the previous text others like the one proposed by J. P. Lange also existed for a long time[4].

One early example is the following equation, first proposed for fuel manufacturing process and later extended to chemical process it allows to estimate the ISBL costs using the total duty of the process section. As said before the Investment (ISBL) equals the CapEx and is used during this work as being the same.

$$Investment\ (ISBL)\ Section\ [M\ \$\ 1993] = 2.9 \times (total\ duty\ [MW])^{0.55} \qquad (2)$$

Where,

Total duty = The energy sum represents the heaters, coolers, heat exchangers as well as pumps and compressors of the distillation or reactor section.

This equation was later updated for 2003 costs by Jean Paul Lange in his paper[5]. Furthermore, some new data and also 15 distillation trains were added. As noticed by Jean Paul Lange [6] the power changed to the very common 0.65 in chemical engineering cost estimations. Although in his paper J. P. Lange already represents an estimation to obtain 2014[1] Investment values, for this research the cost estimation was always regarding the year of 2003, making this year a midterm in between 1993 and more recent investment costs that were used in this research.

$$Investment\ (ISBL)\ Section\ [M\ \$\ 2003] = 2.0 \times (total\ duty\ [MW])^{0.65} \qquad (3)$$

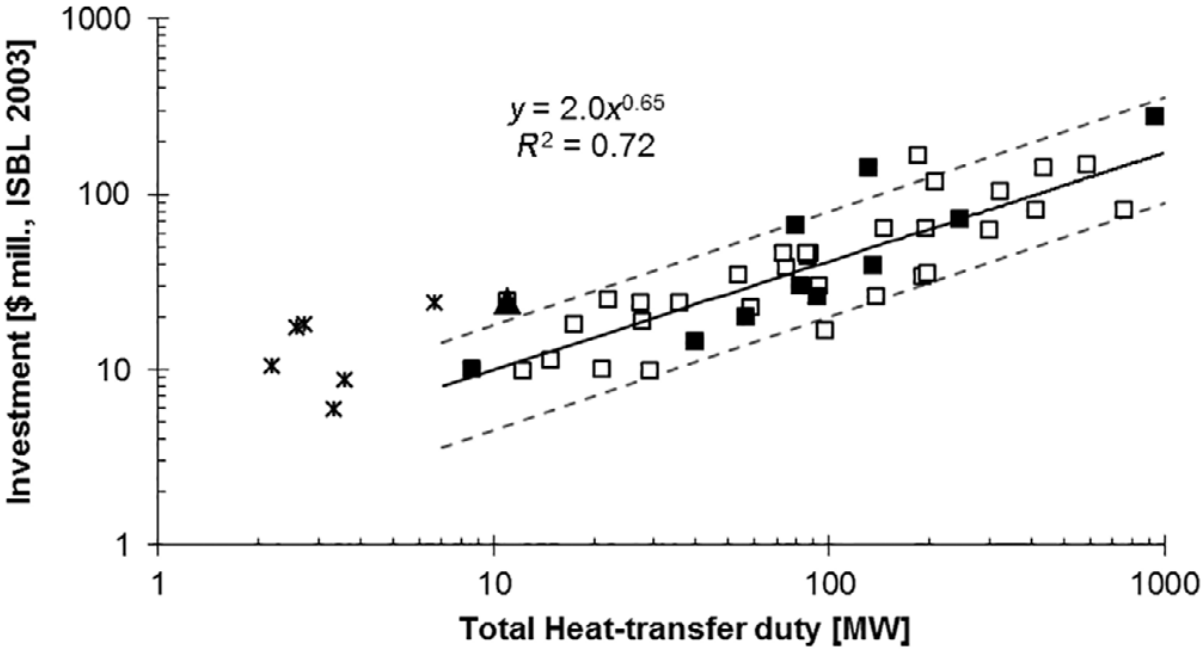

Figure 1.1 Correlation CapEx (ISBL) with Total Heat-transfer duty[1] (open symbols: data from [7] updated to 2003; closed symbols: new distillation sections; stars: units with <10 MW that have benn excluded from the correlation; dotted lines: capex -50% and +100% of the correlation), graph taken from J. P. Lange[1].

This equation shows significant accuracy between -50% and +100% and a lack of the same for sections with heat-transfer duties under 10 MW [1].

At his point it is clear that the cost estimations for a specific section of a process (reaction/distillation) can, up to a certain accuracy, be defined by its energy transfer and with the help of this equation.

This opens the door for the correlation use, which allows us to estimate the duty needed for a distillation section in some minutes, never more than several hours, allowing then to quickly arrive at the cost using the above stated equation.

In order to use the distillation resistance few, and easily obtainable information's are needed: the feed composition, feed flow and the boiling points of the compounds of the mixture.

The assumptions for the use of this equations are that:

- The compounds to be distilled are responsible for the majority of the required duty inside the distillation column (reboiler/condenser);
- The bottom stream, the non-condensable and heating to/from distillation temperature are not significant for the total duty needs;
- All the compounds in the mixture have a similar heat of vaporizations on a weight basis of 0.5 GJ/t, and only some few known Outliers exist;
- The difference in between the boiling points and the size of the distilled stream determine the duty needed to operate the column;

Explaining the concept of the distillation resistance in a simple form: a black box is drawn around all the distillation columns that aren't interrupted by any other equipment and represent the distillation section as seen underneath. Important to point out that for this estimation, in contrast to equation 2 and 3, the heat exchanger and pumps are left outside of the section.

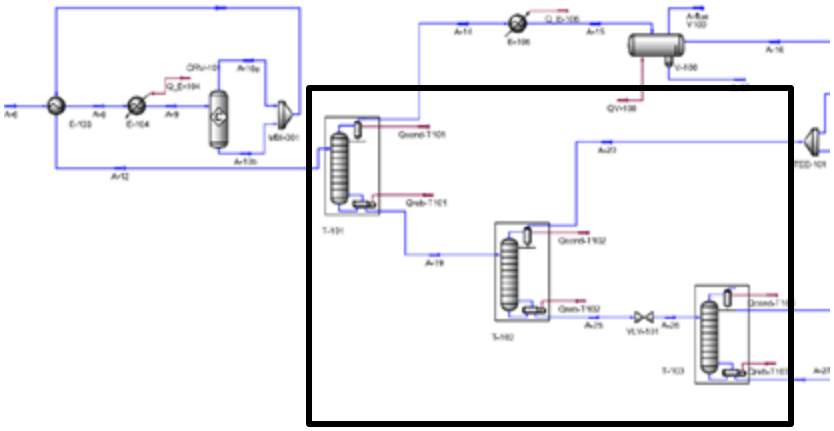

Figure 1.2. Representative Black Box of the distillation section, all the distillation columns in a sequence are lumped together

These columns in the train are lumped together to obtain one large theoretical column and separated in form of the imaginary black box from all the rest of the process. For this reason, just distillation trains that are not disturbed by any other equipment like a reactor, extraction columns or similar are used. Finally, all that is known is the stream that enters the 1st column and the desired separations at the end of the black box, like seen in the image below.

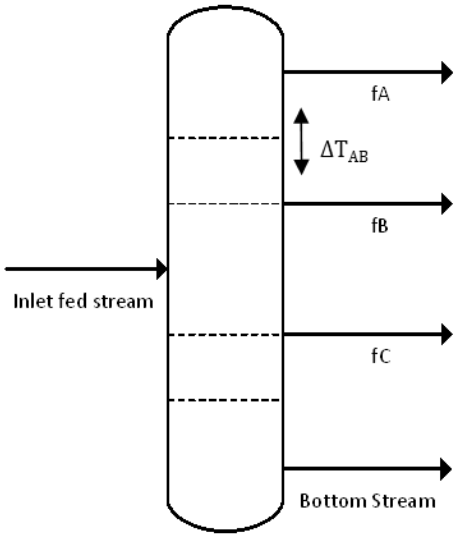

Figure 1.3 Theoretical distillation train lumped in one column, adapted from J. P. Lange[1]

Having determined the black box the distillation resistance can be calculated in the following way:

1. Organize the compounds (fraction of compounds) to be separated in a column by increasing boiling points as how they would leave the column represented above, in a column;
2. In the next spreadsheet column multiply the feed composition wt % of each compound x100 for convenient values for the resistance;
3. In the following spreadsheet column calculate the boiling point difference ΔT_{AB} from the compound(s) to be separated from heavier one(s);

After having prepared these calculations the distillation resistance equation can be applied.

$$\Omega_{feed}\left[\frac{1}{ºC}\right] = \sum \frac{\text{fi}[\text{wt\%}]\ \text{x}\ 100}{\Delta T_{AB}\,[ºC]} \qquad (4)$$

Where,

ΔT_{AB} = Difference in between the boiling points of the compounds to separate

f_i = feed composition being separated in weight percentage

Plotting the energy of the section, GJ/t_{feed}, in function of the distillation resistance for the firing duty (reboiler) and the total duty which contains as well the condenser energy.

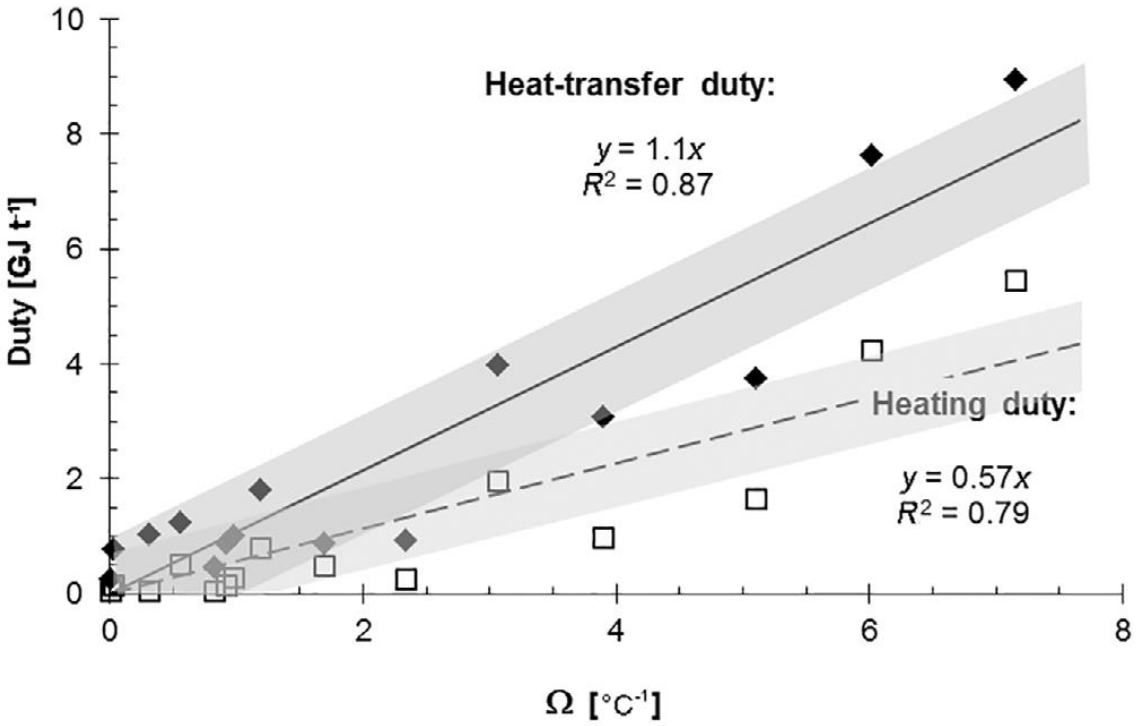

Figure 1.4 Duty Resistance Correlation from J. P. Lange[1] , black points represent the total duty and the white points the firing duty (reboilers)

Looking at the trendlines from the figure, the duty for the separation process can quickly be obtained with the following equations.

$$Firing\ duty\ \left[{}^{GJ}/_{t_{feed}}\right] = 0.57 \times \Omega_{feed} \qquad (\pm 0.7) \qquad (5)$$

$$Total\ duty\ \left[{}^{GJ}/_{t_{feed}}\right] = 1{,}1 \times \Omega_{feed} \qquad (\pm 1) \qquad (6)$$

The total duty represents approximately double of the heating duty, which is explained by the fact that the reboiler is transferring energy to the condenser, shown in appendix D, 69.
Having now a quick way to estimate the duty, the next step is to correlate the same to the costs like it is done in the usual cost – duty estimations, reaching at this point the final step.

Easy accessible data/quick calculations → Duty → **Cost**

As seen already in equation 3 it is possible to correlate the duty to the cost of a process section. Since the goal is to have a quick estimation, the equation is rearranged to have directly the distillation resistance feed as variable to obtain the investment cost. The whole conversion can be found in the appendix A at page 65.

Rewriting the following equation is presented,

$$Investment\ (ISBL)\ Section\ [M\$\ 2003] = 0.24\ x\ (feed\left[\frac{kt_{feed}}{a}\right] x\ \Omega_{feed})^{0.65} \qquad (7)$$

Where,

a (unit) = represents year (annum)

kt_{feed} (unit) = kiloton of feedstream

Being the CapEx value just a part of the total costs, also the OpEx needs to be estimated in order to arrive at the total distillation Cost: ISBL + OpEx. Nevertheless, not all the feed has a market value and for that reason it is also important to normalize the resistance per sellable product like shown next.

$$\Omega_{prod}\left[\frac{1}{º C}\right] = \frac{\Omega_{feed}}{wt\ \%_{prod}} \qquad (8)$$

Where,

$wt\ \%_{prod}$ = percentage of sellable product

The percentage to divide the distillation resistance feed is defined by the amount of sellable product entering the 1st distillation column. In this form the cost and energy required is always associated to the value that is achieved from the separation.

Using this new parameter of the distillation resistance and calculating the OpEx and ISBL as seen in the appendix B, page 66, the equation for the total distillation cost is obtained.

$$Distillation\ cost\ \left[\frac{\$2003}{t_{prod}}\right] = \left(\frac{60 \times {\Omega_{prod}}^{0.65}}{Capacity\ \left[\frac{kt_{prod}}{a_{prod}}\right]}\right) + 3 \times \Omega_{prod} \qquad (9)$$

Where,

Capacity = output rate per year of the product

Ω_{prod} = distillation resistance of the product

This equation represents well the chemical process costings: as higher the amount of produced product per year as lower the costs per unit are, due to the economy of scale. Furthermore, as trickier the separation or as lower the % of produced product in the feed stream is as higher are the distillation costs. Representing this equation in function of the Ω_{prod} for fixed distillation cost prices it becomes more evident what has been said before.

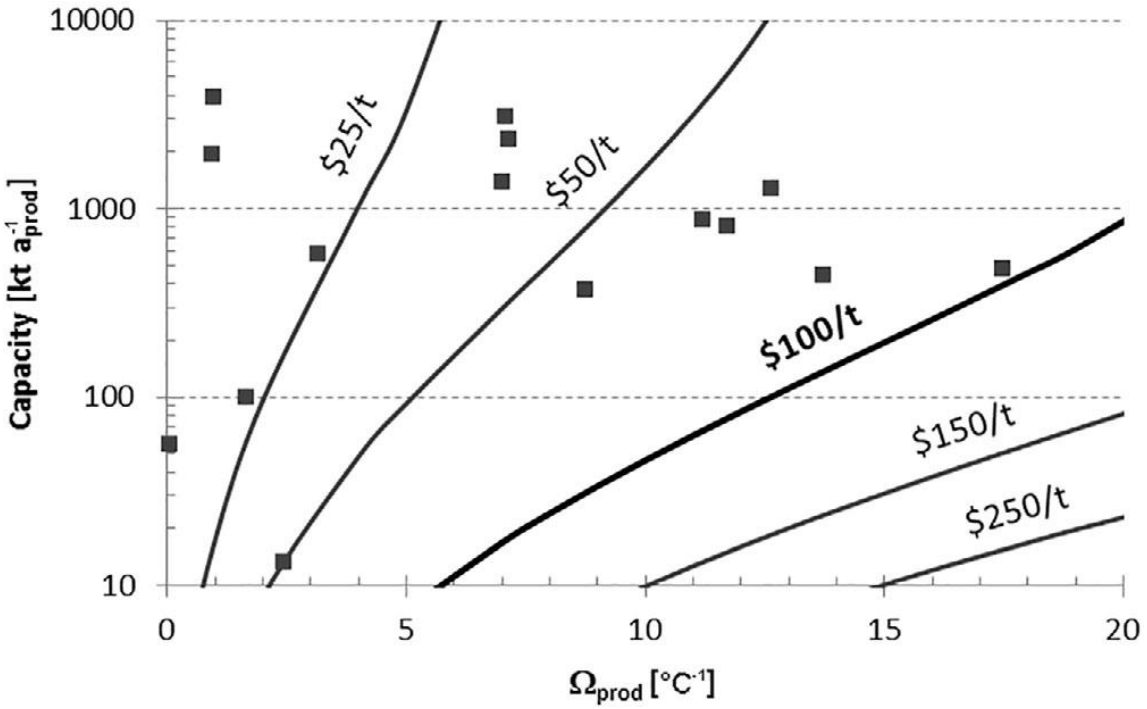

Figure 1.5 Distllation cost equation following economy of scale[1], using the equations elaborated from J.P. Lange for the different distillation costs, calculations on page 67 in the appendix B

The distillation costs lines decline in its steepness, in function of the capacity. With this equation J. P. Lange defined \$100/t as the prohibitive limit for a distillation cost [1].

1.3 Reaction Section (a beginning of a total process estimation)

With the goal in the future to, in some extend, be able to estimate the whole process, a beginning was attempted to also estimate the reaction section. Likewise, a try is made to fit the section in a black box separating it from the rest of the process. The segment should include the reactor and the heat exchangers that bring the stream to and from reactor temperature. Assuming that the stream is heated from and back to 30ºC and that the energy for pumps are neglected. Simplifying the following energy contributions for the section are estimated.

$$Reaction\ Section\ \left[\frac{GJ}{t_{feed}}\right] = HE\ \left[\frac{GJ}{t_{feed}}\right] + \ Reactor\ \left[\frac{GJ}{t_{feed}}\right] \qquad (10)$$

Looking at the first term of the equation, the heat exchanger, similar simplifications are applied like seen for the distillation resistance. Being the assumptions as followed:

- No phase change happens during the heating or the cooling (only sensible heat is present);
- All the compounds have a similar specific heat capacity of 2 [kJ/Kg.ºC];
- The feed stream is brought to reactor temperature from room temperature (30ºC) and the product stream is brought back to room temperature;

With the following traditional equation as a starting point.

$$Mass\ \left(\frac{kg}{h}\right) \times Cp\left(\frac{kJ}{kg.ºC}\right) \times dT = Duty\ (\frac{kJ}{h}) \qquad (11)$$

Where,

C_p = Heat Capacity

dT = Heat variation of the mass

Using 2 ($\frac{kJ}{kg.ºC}$) as the reference standard heat and multiplying the heat exchange by factor X, to have the heating and the following cooling, the equation is obtained.

$$feed\ stream\ \left(\frac{kg}{h}\right) \times 2\left(\frac{kJ}{kg.ºC}\right) \times (T_{reactor} - T_{room}) \times X = Duty\ (\frac{kJ}{h}) \qquad (12)$$

Where,

T_{room} = Room temperature considered 30ºC

X = Variable regarding the heating and cooling from the stream considered 2 initially

This proposed equation was as said the starting point, but after the research it was clear that this showed to be an overestimate for the duties. For this reason, two alternative pathways were also checked upon.

The idea was to change the equation in the following way, adding one estimation where total heat integration is assumed and with this the 2 factor, for the heating and cooling, is left out of the equation, meaning that the product stream heats the feed stream. And a 3rd one where the 2 factor is substituted by 1.5 assuming that only one equipment is heat integrated and the other is not. For all the three different alternatives the equation is the same and only the factor at the end to 1 (Full heat-integration), 1.5 (Partial heat-integration) or 2 (No heat-integration) is changed.

For the reactor heat the equations to be used are more straight forward and no big deviations should occur. For this estimations no differentiation was made for the reactor type. Going from the Hess law the heat of reaction for each reaction is calculated as followed.

$$\sum(\Delta H_{Reaction}\frac{kJ}{mol} \times Mol\ formed\ \frac{kmol}{h}) \times 1000 = Reactor\ Duty\ (\frac{kJ}{h}) \quad (13)$$

Where,

$\Delta H_{Reaction}$ = Enthalpy for the reaction

Mol formed = mole of product formed

The sum of all the reaction heats inside the reactor gives the energy needed to be removed or provided for a reaction to happen and is defined as reactor duty. Sometimes this value is small and for that reason no heating or cooling occurs, instead the reactor is let to increase or decrease in temperature itself, seeing that no big temperature rise/drop can happen. This research topic in comparison to the distillation resistance was analyzed in a shorter period of time and no equations from earlier research were available to compare with.

1.4 Information source

One of the goals in this research was also to test how the correlation would behave for different datasets. In the case of Jean Paul Lange the information was obtained from process flow schemes within Shell [1], as what this analysis applies the information came from PPD´s, Process Plant Design, made by the students of the University of Twente. The PPD is a report analyzing the techno-economic feasibility of a process touching on themes like the market of the product, the technology of the process, equipment, flow sheeting, control, safety and finally an economical evaluation to decide upon the profitability of the whole project. One of the major tools used for this reports is a program called *Unisim* to simulate the process. In the following table the main differences are illustrated.

Table 1.1 Comparison in between the two differente data set of the research from J. P. Lange [1] and the ones used for this research provided bt the University of Twente

	J.P.Lange	Research
Source	Shell	PPD
Biggest distillate stream (wt %)	98	92
Biggest process size (MT/year)	11	2
Smallest ΔT (ºC)	5	18

2 Methodology

2.1 Study case

After trials and improvements, the following methodology for the distillation resistance calculation was obtained. This approach is set out for the extraction of the provided data set given the PPD (Process Plant Design) and its associated *Unisim*. The guidelines are set up in different parts to make them easier to follow:

- Choosing a PPD
- Extracting Information from the PPD
- Extracting Information from the *Unisim*.
- Calculation of the distillation resistance
- Special cases

2.2 Choosing a PPD

The PPD's used had to fulfill the following criteria:

- Have more than one Distillation Column in the separation train;
- The train needed to have only simple Distillation Columns (one extractive Column, included in a train, was also analysed with success);
- Conventionally no Azeotropes should form in the Column (some columns from the data had cases where azeotropes where formed);

Having fulfilled this criteria, the following PPD were chosen: 163, 184, 187, 189, 193, 196, 199, 201, 203 and 207, corresponding to the processes shown in the table.

Table 2.1 10 different PPD's of the research and their process names organized by number

Number	Process
163	Alkylation of Benzene with Ethanol to Ethylbenzene
184	Palmitoleic Acid to produce 1-Octene
187	HPPO – Propylene Oxide production from Hydrogen Peroxide
189	Hydrotreated Vegetable Oil
193	Producing Green Styrene by Acylation of Benzene
196	Amino Acids to Amino Alcohols
199	Upgrading Acetic Acid to Acrylic Acid
201	LNG Recovery
203	Biofuels from Pyrolysis Oil Via Gasification
207	Dimethyl carbonate from methanol and CO2

Since along the research all the PPD's are going to be referred as to their number for simplicity reasons, this page number is important to keep in mind in case the process name is desired.
Some of the mentioned PPD's who did not correspond perfectly to the criteria were also tested to see the strength, limits and also just for mere quantity reason, to have more data available to be compared to each other.

2.3 Extracting Information from the PPD

Beside Process 163, for being an older PPD with no *Unisim* file, all the other PPD's had their information extracted in the same way. The fact that the information from 163 were taken directly from the written report, could have led to less trustworthy values, numbers could have been mistaken by simple typing mistakes from the PPD editors, like seen in some newer PPD's. Nevertheless, from the results this did not seemed to be the case here. For the newer data, this possible error factor is eliminated by taking the information directly from the simulation of *Unisim*.

In this way two slightly different approaches were used: The Data for the 163 PPD of the written report in question not represented in this work for confidential reason. For all the other PPD's the mass balances, boiling points, feed compositions and conditions were taken from *Unisim*.

Furthermore, from the written report, data for the CapEx correlation calculations were also extracted for all the PPD's. This information was only explicitly represented for some processes, since for some the costs were summed together. Nevertheless, the following processes had their cost information independently presented and could be used for the research – 163, 184, 187, 189, 199, 207.

2.4 Extracting Information from the *Unisim*

All the processes beside 163 had the same information extracted from *Unisim* which more detailed was:

- The total feed stream, always for the 1st Distillation Column;
    - If a compound stayed in the gas phase (non-condensable), ex. PPD - 184, they were not considered for the mass amount to be separated;
- The mass flow from the simulation would always be the "total" ones, which is the sum of the vapour phase and liquid one, seen that they would only not be used if the compound(s) were in the gas phase entering and exiting the Black Box;
- The atmospheric boiling points, represented as NBP (Normal Boiling Points);
- The pressures and temperatures for the inlet feed stream;

- Duties for the equipments, reflux ratios, number of stages, temperatures at the entry stage, condenser and reboiler for all the distillation columns in the train;

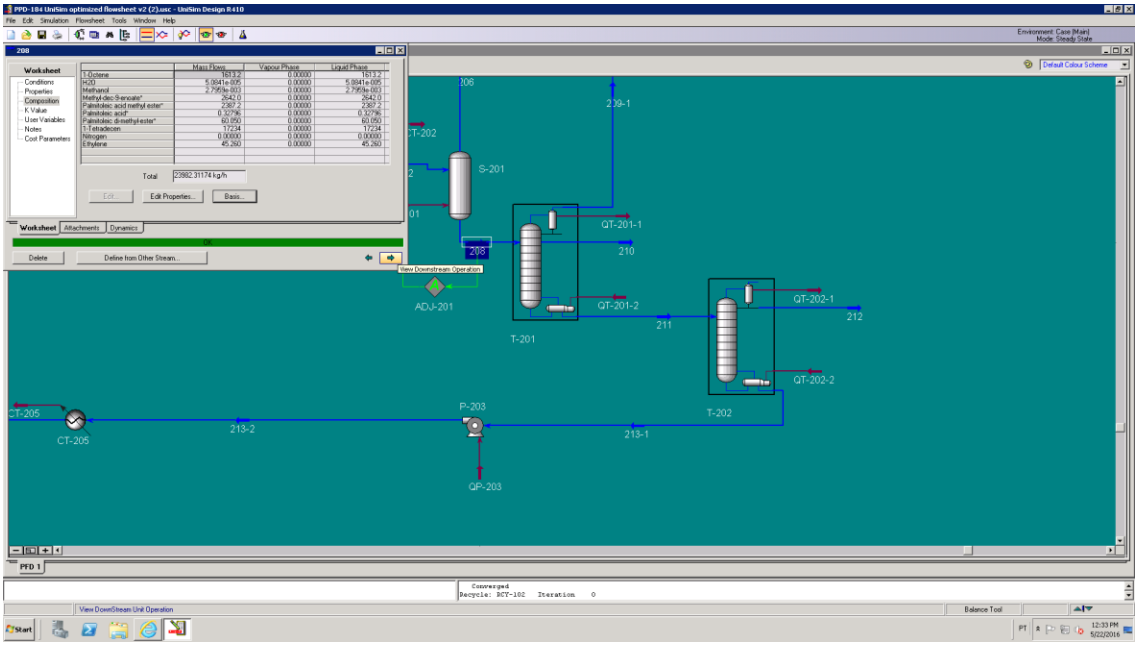

Figure 2.1 *Unisim* image of an example information extraction for the distillation section, extracting the feed composition

In order to simplify the calculations, the information was transferred already in the subsequent form.

Table 2.2 *Unisim* Data of the inlet feed stream composition multiplied by 100 and organized by increasing boiling point (Example PPD - 184)

Compound	Flow [ton/h]	Feed wt % [x100]	NBP [ºC]
Nitrogen	0	0	-196
Ethylene	0	0	-104
Methanol	0	0	65
H2O	0	0	100
1-Octene	2	7	121
Methyl-dec-9-enoate*	3	11	228
1-Tetradecen	17	72	251
Palmitoleic acid methyl ester*	2	10	309
Palmitoleic acid*	0	0	337
Palmitoleic di-methyl-ester*	0	0	359
Total	**24**	**100**	

To be able to have a better perception of the distillation columns the succeeding data were also obtained, having included in the table also the economic numbers from the written report, not yet updated for the year of 2003 and also the equipment costs, not yet representing the ISBL values. Likewise, the duties were converted to GJ/h.

Table 2.3 Distillation Columns Flowsheet Information (Equipment costs and not ISBL), process 184 taken from Unisim to have a better global image of the conditions and costs (Example PPD – 184)

	T-201	**T-202**
Pressure (bar)	0,3	0,2
$T_{Condenser}$ (ºC)	80	167
$T_{Reboiler}$ (ºC)	199	190
Reflux Ratio	7	10
Stages	10	43
Reboiler (kJ/h)	8852177	6294786
Condenser (kJ/h)	647739	6956732
Total (kJ/h)	**9499916**	**13251518**
Reboiler (GJ/h)	8,9	6,3
Condenser (GJ/h)	0,6	7,0
Total (GJ/h)	**9,5**	**13,3**
Reboiler (M$ 2012)	0,02	0,02
Condenser (M$ 2012)	0,05	0,05
Column (M$ 2012)	0,12	0,45
Total CapEx (M$ 2012)	**0,2**	**0,5**

2.5 Calculation of the Distillation Resistance - Duty

At this point all the information to use is gathered and the correlation can be used. To do this the difference in boiling points of the compounds to be separated was calculated and resulted in the following table.

Table 2.4 Distillation Resistance calculation, feed composition organized per separated mixtures, boiling point difference calculations as well as final distillation resistance equation use and result (Example PPD – 184)

Compounds	**Feed wt % [x100]**	**NBP [ºC]**	**ΔT_{AB} [ºC]**	**Ω_{feed} [100/ºC]**
Ethylene (gas)	0,2	-104	225	-
1-Octene	6,7	121	107	0,06
Methyl-dec-9-enoate	11,0	228	23	0,47
1-Tetradecen + Heavier	82,2	251		
Total	**100**			**0,54**

The bottom stream is a sum of all the compounds that are leaving at the bottom, lumped together in this case the Palmitoleic Acid Methyl Ester and the 1-Tetradecen, both are recycled to the reactor to obtain more product.

Having calculated the distillation resistance, the results need to be compared to the values from the simulation (Flowsheet) to obtain their accuracy of the duty estimations: total (reboiler + condenser) and firing (reboiler).

Table 2.5 Distillation Resistance Results using the equations presented in the introduction and compared to their Unisim results obtaining the absolute deviation (Example PPD – 184)

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,6	0,3	0,3
Total (GJ/t_{feed})	1,0	0,6	0,4

2.6 Special cases for the distillation resistance

2.6.1 Average Boiling Point for a fraction

In order to have a strict and with that easy to follow guideline some aspects for the calculations had to be determined, being this the case in lumping situations. A lot of times in a separation in a distillation train not every compound gets separated uniquely. For example: waste, reactants or products that are a range of different molecules are lumped and separated as a fraction. For these specific cases a rule must be made in how to define the boiling point of the fraction that is being separated.

From the results, the following approach tended to have the best outcome in accuracy on the results along this research.

Exemplifying with process 189, a typical petrochemical refinery process separating LPG, Naphtha, Kerosene and Diesel the information obtained from *Unisim* would look like followed.

Table 2.6 Feed Composition not lumped together and expressed for each compound, organized by increasing boiling points (Example PPD – 189)

Compound	Flow [ton/h]	Feed wt % [x100]	NBP [ºC]
Propane	0	0,0	- 42
n-Butane	0,1	0,1	-1
n-Pentane	0,5	0,5	36
n-Hexane	0,6	0,6	69
n-Heptane	0,6	0,6	98
n-Octane	0,6	0,6	126
n-Nonane	0,7	0,7	151
n-Decane	0,7	0,7	174
n-C11	0,7	0,7	196
n-C12	0,7	0,7	216
n-C13	5	4,6	235
n-C14	4	3,7	254
n-C15	23	23,3	271
n-C16	15	15,4	287
n-C17	27	27,5	302
n-C18	14	14,1	317
n-C19	6	6,2	331
Total	**99**	**100**	

Using this information and separating into the fractions, with the following equation, the average boiling points can be obtained.

$$NBP\ of\ the\ Fraction\ = \sum (\frac{Compound\ \left[\frac{ton}{h}\right]}{Fraction\ \left[\frac{ton}{h}\right]} \times NBP[ºC]) \qquad (14)$$

Where,

NBP = Normal Boiling Point
Fraction = Lumping of several individual compounds into a mixture

The fraction represents a product stream consisting of a mixture of different compounds. In the table an example of a normal fraction is represented.

Table 2.7 Lumping a fraction in this case naptha consisting of the shown different compounds, its feed composition and boiling points (Example PPD – 189)

Naphtha	Flow [t/h]	Feed wt %	NBP of Interval [ºC]
n-Pentane	0,5	22%	8
n-Hexane	0,6	25%	17
n-Heptane	0,6	26%	26
n-Octane	0,6	27%	34
Total	**2,3**	**100%**	**60**

Using the resulting fraction boiling points, the distillation resistance can be calculated as demonstrated before. This makes sense especially for cases like the one shown above as there are no highly critical product specifications needed and cross contamination is accepted.
The products that have high specifications associated usually are separated as a sole compound without being a mixture and with that do not need this calculation.

2.6.2 H_{vap} correction factor

Another issue that presented itself during the research, although it was in some point already expected, is the difference in the enthalpy of vaporization of the compounds. One of the assumption for the use of the equation is that the H_{vap} of all the compounds would need to have a similar value on a mass basis. Compounds that would fall outside of the usual determined values, would need, with a correction factor, to be fitted. The solution found was to use the proportion in between the usual H_{vap} value of 0,5 GJ/t_{feed}, compared to the one from the outliers.

$$\Omega_{feed}\ (H_{vap})\ = \Omega_{feed} \times \left(\frac{H_{vap[\frac{GJ}{ton}]}}{H_{vap(reference)[\frac{GJ}{ton}]}}\right) \qquad (15)$$

Where,

H_{vap} = Enthalpy of vaporization of the compound

$H_{vap(reference)}$ = Reference enthalpy of vaporization (0,5 GJ/t_{feed})

By using this correction factor the resistance is increased or decreased in function of the outlier´s H_{vap} shown in the figure.

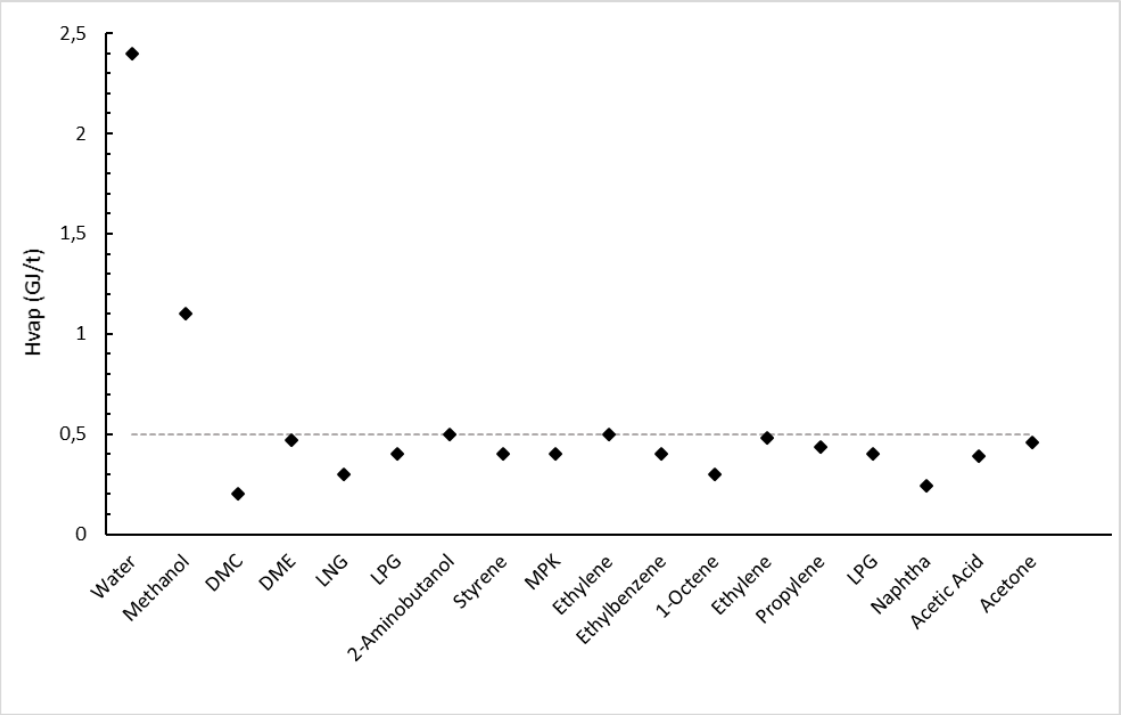

Figure 2.2 H_{vap} comparison of majority of the compounds present in the PPD's with the mean of 0,5 GJ/T_{feed} (*Unisim* data)

As it can be seen water and methanol are concerning their H_{vap} values outliers compared to the majority of the compounds and would in theory need to have the H_{vap} correction factor being used.

2.6.1 Ω_{prod}

To calculate the distillation resistance of the product all compounds with a market value that are being distilled are summed to give the product wt % to use equation 9 on page 8. This percentage is not always equal to the desired product of the process, as it can also have compounds from side reactions that have a market value and can in this way can be sold too.

2.7 Duty Calculation of the reaction section

For the reaction section the same PPD's were further analysed. No other PPD's beside these ones were analysed since the time for this part of the research was limited.

With this estimation a global view could be presented of the already shown processes.

Process 163 due to the lack of an *Unisim* file and process 201 which is a mere separating process without any reactor, were taken out of the dataset.

To begin, some parameters that were important for the following calculations were extracted from *Unisim* and are shown in the table.

Table 2.8 Parameters for the reaction section calculations taken from the *Unisim* file (Example PPD – 203 first section)

Parameters	
Inlet feed stream (kg/h)	**Reactor T (ºC)**
209443	250
Inlet feed stream (ton/h)	**Product stream (ton/h)**
209,4	31,5

2.7.1 Calculation of the heat exchanger duty

Looking at the heat exchanger part of the reaction section a 1st obstacle, also the major one, presented itself. A decision needed to be made where the Black Box for this section part would be drawn. After some discussion on this topic, it was decided to include the heat exchangers that were in an immediate surrounding of the reactor. All the heat exchangers that were further away were considered to be integrated in a possible recycling section, still to be determined at this point in time.

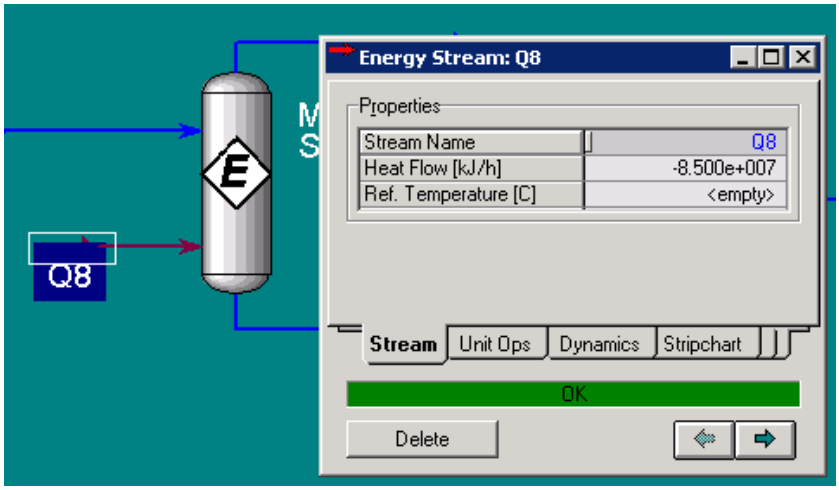

Figure 2.3 Reboiler duty for the distillation column (Example PPD – 203), (*Unisim* Data)

In this 1st approach no correction was made for any of the different Cp values and all considered to be the same around the 2 kJ/kg.ºC mark, which is almost accurate as can be seen in the figure.

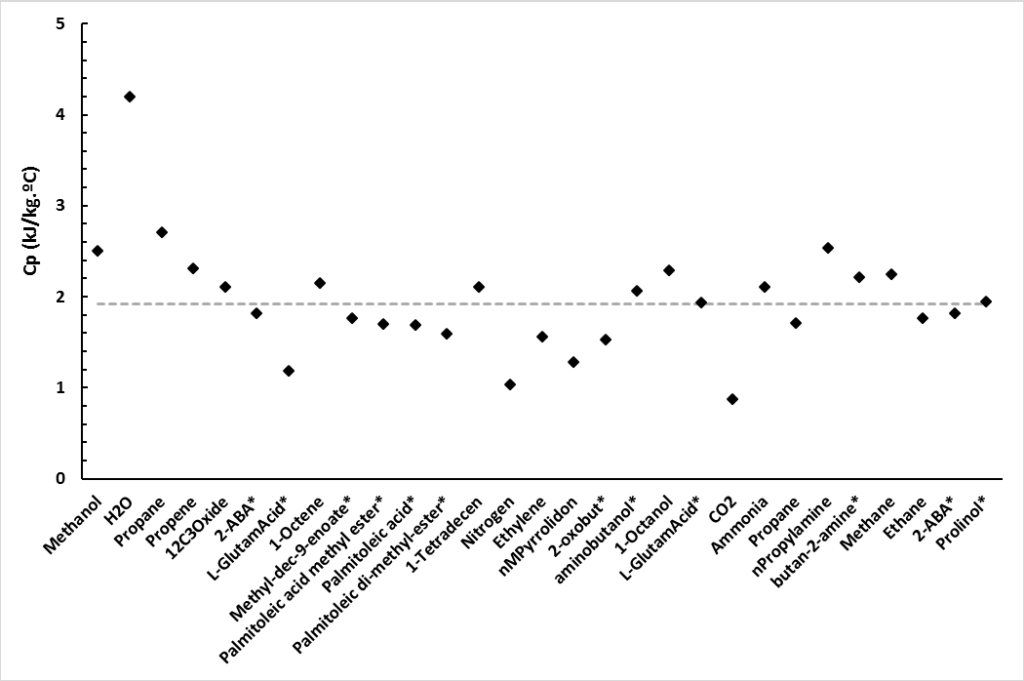

Figure 2.4 Cp's used by *Unisim* for the simulation for each compound compared with the mean of 2 used in the calculations (*Unisim* Data)

As it can be observed above the majority of the values situate themselves around the 2 (kJ/kg.ºC) mark. Again, like already been seen for the H_{vap}, water and methanol represent larger values. The majority of these numbers are for the liquid Cp. The values were extracted from the *Unisim* files, meaning that they were used to do the simulations.

Moving on to the calculations, the inlet feed stream into the reactor and the reactor temperature, shown in table 2.8 previously, were used for equation 13 on page 10.
After having the duty for the heat exchanger calculated in (kJ/h), the value is also divided by all the sellable products to have a result in GJ/t_{prod}.
This approach as stated before neglects the evaporation of the feed/product stream and with this its associated heat. An example for process 203, section 1 is shown in table 2.9.

Table 2.9 Reaction section calculations heat exchangers, process 203-1

Heat Exchanger	
***Unisim* (kJ/h)**	**Estimation (kJ/h)**
196301979	92155017
***Unisim* (GJ/t_{prod})**	**Estimation (GJ/t_{prod})**
6,2	2,9

2.7.1 Calculation of the reactor duty

As what the reaction part concerns, equation 14, page 11, is used. In order to decrease the time needed for the calculations and after having rechecked the values with the literature for some processes, the reaction heat and the mol formed were taken directly from the *Unisim* data as seen underneath for each reaction. The *Unisim* values for the mol formed represented, already have into consideration the conversion of the reaction.

The reaction heat was converted into kJ/mol subsequently in the *excel* spreadsheet.

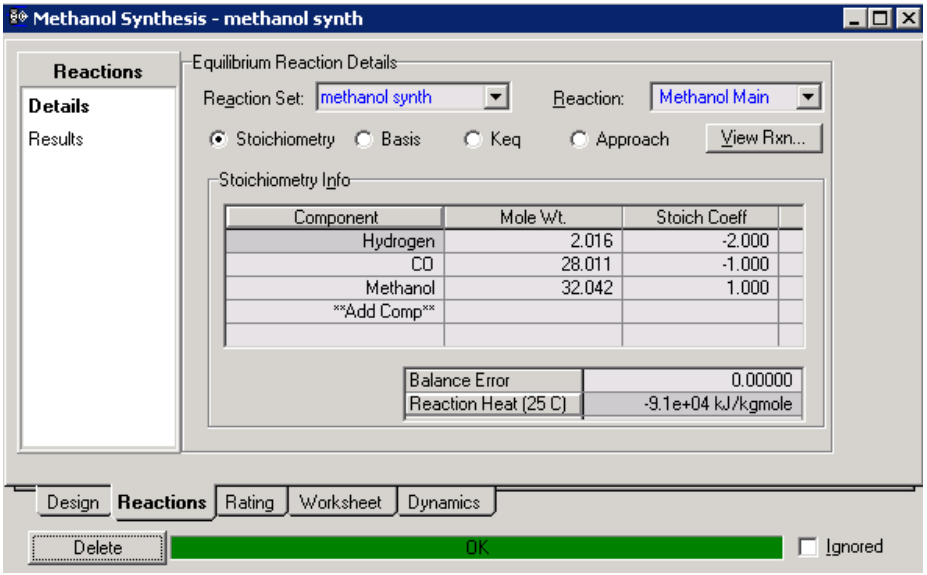

Figure 2.5 Mol formed and reaction heat (Example PPD 203 1st section), (*Unisim* Data)

Next, the conversion in mol for the limiting compound, as well as the mol used of the same compound (Rxn Extent), were also copied into the excel spreadsheet.

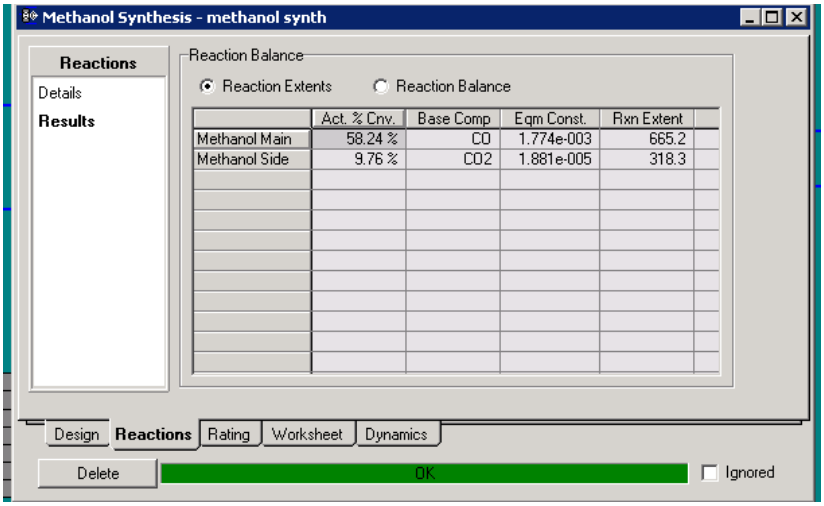

Figure 2.6 Mol of the limitant compound (Rxn Extent) and conversions (Example PPD 203 1st section), (*Unisim* Data)

This approach saved precious time that would have been needed to be spent searching for formation heats and calculating the heat of reaction for each of the ones that are happening in the reactors, as well as the conversions.

The following table represents all the reactions occurring inside the reactor, in this case the 1st reactor of process 203. The final heat of reaction is the result of using equation 14, on page 11.

The total sum of heat generated or removed in the reactor can be found at the bottom right of table 2.10 summing all the individual reaction heats.

Demonstrating again the use of equation 16 for the methanol synthesis side reaction in this case.

$$319\left[\frac{kmol}{h}\right]\times 1000\left[\frac{mol}{kmol}\right]\times -49\left[\frac{kJ}{mol}\right]=-15706692\ kJ/h \qquad (16)$$

Table 2.10 Differente reaction happening in the 1st reactor of process 203, the produced kmol/h have already the conversions included, the total heat is the sum of all the individiual reaction heats

Reactions			
Compound/Reaction	***v***	**Produced [kmol/h]**	
Methanol Synthesis Main reaction			
Hydrogen	-2		**Conversion % (mol)**
CO	-1		58%
Methanol	1	665	**$H_{reaction}$ (kJ/mol)**
			-91
			Final Heat of reaction (kJ/h)
			-60340756
Methanol Synthesis side reaction			

Methanol	1	319	**Conversion % (mol)**
H2O	1	319	10%
CO2	-1		**$H_{reaction}$ (kJ/mol)**
Hydrogen	-3		-49
			Final Heat of reaction (kJ/h)
			-15706692
		Total Mol formed	**Total Heat in the Reactor (kJ/h)**
	Sum	**1302**	**-76047447**

To clarify, the value of the *Unisim* data for the reaction section shown next in the table, which are compared with the estimation values, are the ones the reactor is actually using in utility in order to keep the reaction working, it should not be misunderstood with the heat that is generated or removed in the reactor. Summing up all the duties for the different reactions insight the reactor, and normalizing in the same way as it has been done before for the heat exchangers

The following table shows the results for the reactor section estimation for the mentioned reactor.

Table 2.11 Results table for the reactor estimation compared to the energy used in the simulation for the reactor in utility (Example PPD – 1st section 203)

Reactor	
***Unisim* (kJ/h)**	**Estimation (kJ/h)**
-85025140	-76047447
***Unisim* (GJ/t_{prod})**	**Estimation (GJ/t_{prod})**
-2,7	-2,4

By estimating the heat in the reactor a decision needs then to be made on whether an integrated heat transfer unit should be installed directly in the reactor or only in the heat exchangers. The following table sums up the results to be compared with the *Unisim* data.

Table 2.12 Results for the reaction section estimation values compared to the Unisim normalized per ton of product and the absolute deviation in between them (Example PPD – 1st section 203)

Results			
	***Unisim* (GJ/t_{prod})**	**Estimation (GJ/t_{prod})**	**Absolute Deviation**
Heat Exchanger	6,2	2,9	3,3
Reactor	2,7	2,4	0,3
Sum	**8,9**	**5,3**	**3,6**

2.8 Duty – Cost

2.8.1 Distillation cost

Again to clarify and avoid misleading thoughts, the capacity used for the distillation costs calculations seen in figure 1.5, on page 9, and also in this research are the ones of the desired product, meaning the output rate of the main product of the plant. After having fixed the distillation cost, the capacity of the plant and the Ω_{prod} are used as variables to discover if the prohibitive limit of 100 $/t is reached or not.

Regarding the OpEx topic for this research, it was not analysed since the values in the PPD were not specified in a way to result in trustworthy results.

2.8.2 CapEx

As said before just the values for the costs from the PPD´s were used where they were specifically reported and no estimations needed to be done. Having those values first thing was to actualize or capitalize them to the year of 2003 to match the ones of J. P. Lange. To do this the CEPCI (Chemical Engineering Plant Cost Index), for each process and its year was applied as followed, the table for each process can be found in appendix G, page 77.

$$Cost_{2003} = Cost_X \times \left(\frac{CEPCI_{2003}}{CEPCI_X}\right) \quad (17)$$

Where,

$Cost_x$ = Cost of the equipment of the PPD that is going to be capitalized to the year of 2003

Also the inlet feed stream of the column was changed to kt/a, different than in Portugal with 8400h, the working hours per year per plant were considered being 8000h.

$$Feed\ \left(\frac{t}{h}\right) \times \frac{8000}{1000}\left(\frac{h}{a}\right)\left(\frac{kt}{t}\right) = 8\ \times\ Feed\ \left(\frac{t}{h}\right) = Feed\ \left(\frac{kt}{a}\right) \quad (18)$$

The trickier part was the conversion from the purchase costs to their ISBL. The reason for this is the many possibilities there are to do it. It was opted to use the Lang Factor of 4.74, specifically for fluid only process (no solids included), seen that all the process are fluid processing plants. The decision to use this factor was taken by the fact that it is the one most practitioners use[2]. Also other variables to convert the costs to their respective ISBL were tested and are shown in the appendix G, page 77. As explained in the text of chemical engineering principles[2] and seen next the conversions were made.

$$C = F \times (\sum C_e) \quad (19)$$

Where,

C = total plant ISBL capital cost (including engineering costs);

$\sum C_e$ = total delivered cost of all major equipment items: reactors, tanks, columns, heat exchangers, furnaces etc,

F = an installation factor, later widely known as a Lang factor (4,74 for fluid processing plants like the ones from this research)

After having all of these data set the only thing left is to plot the costs in function of the feed (kt/a) x Ω_{feed}.

Going to the reaction section, whereas for the distillation resistance the duty would be obtained from the resistance and then correlate to give the cost, in this case the approach is different.
The process that had exact costs of equipment´s were 187, 189, 193 ,196, 199.
Again the Lang factor of 4.74 was used to convert the units to their respective ISBL costs, after they had been converted in M$ 2003. For the reaction section beside the reactor also heat exchangers costs were summed. Here only the *Unisim* values in MW were plotted in function of the ISBL values in order to again validate equation 3, on page 4.

3 Results and Discussion

3.1 Distillation Section – Duty (Distillation Resistance)

3.1.1 Final results distillation resistance validation

The 1st target of the research was the validation of the method presented in the article of Jean Paul Lange [1] in order to have a quick duty estimation. The parity plot for the total duty shows a good answer for this question, validating it for the majority of the points.

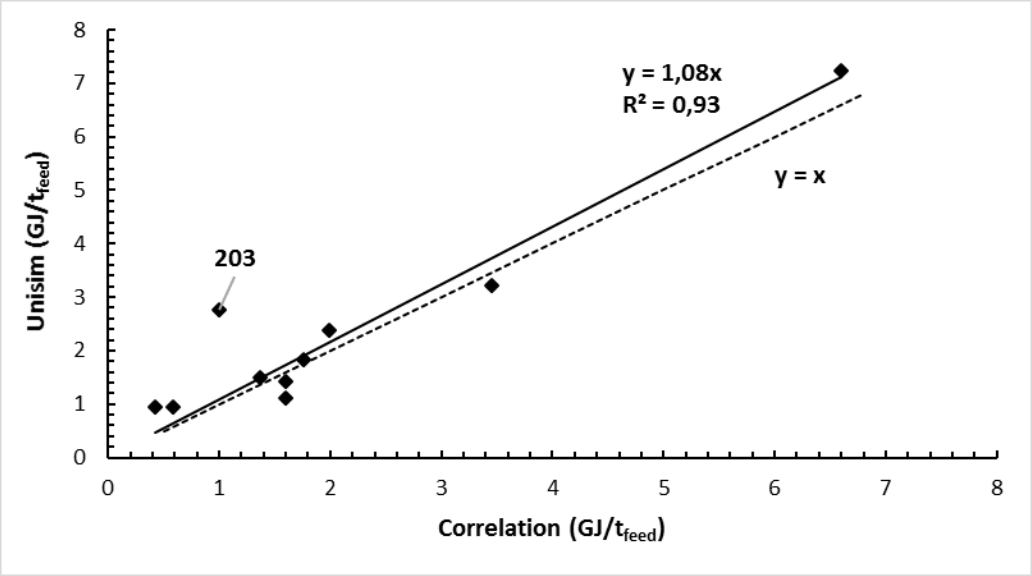

Figure 3.1 Parity plot distillation section (using the H_{vap} correction factor when needed, process 203 the major Outlier), comparing the Unisim values with the estimation using Jean Paul Langes equations

From the figure it is clear to see that the correlation proposed could be validated, representing only process 203 a higher than normal deviation.

Overall the correlation for the common distillation columns train appears to show good accuracy when compared with the *Unisim* simulation by having a standard deviation of 0.45. Nevertheless, a correction needed to be applied for the H_{vap} in process 196, the largest point in duty requirement, for its high amount of water being separated.

Shown again the estimation in the figure, but in this case the normalized by the product stream and organized by process, the difficult separations are easier to identify.

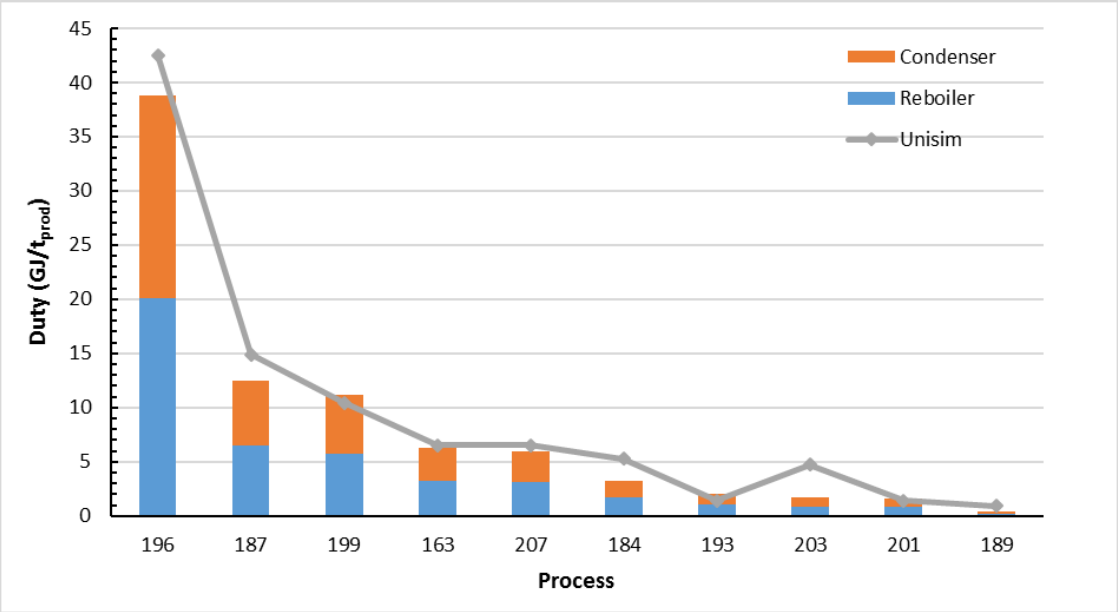

Figure 3.2 Estimation of duty (GJ/t_{prod}) with the distillation resistance and compared with *Unisim*, organized by energy demand and division in between reboiler and condenser duty

A better efficiency of the process can be seen in correlation to the value that is produced with this figure. By having a standard deviation of 2.6 GJ/$t_{prod,}$a good sign of a valid duty estimation is demonstrated. Interesting to notice is the fact that process 187 the production of propylene oxide overtakes process 199 which in the previous graph is the second highest point, showing that less product is obtained for the energy input provided.
This strengthens the idea that the duty should always be normalized per ton of product to give a better perception of the efficient application of the energy.

Overall compared to J. P. Lange the processes at hand showed to be easier, as it could already be seen by having lower distillation resistance values. The fact that the plants are smaller in size also strengths this idea, since a more difficult process is preferable fulfilled in a larger scale to take profit out of the economy of scale.

This and further details about the approach and results, specially how these final results were obtained are going to be presented in this chapter.

3.1.2 1st Results

Using the average boiling point for fractions when needed and not correcting for neither H_{vap} or azeotropes the following first results were obtained.

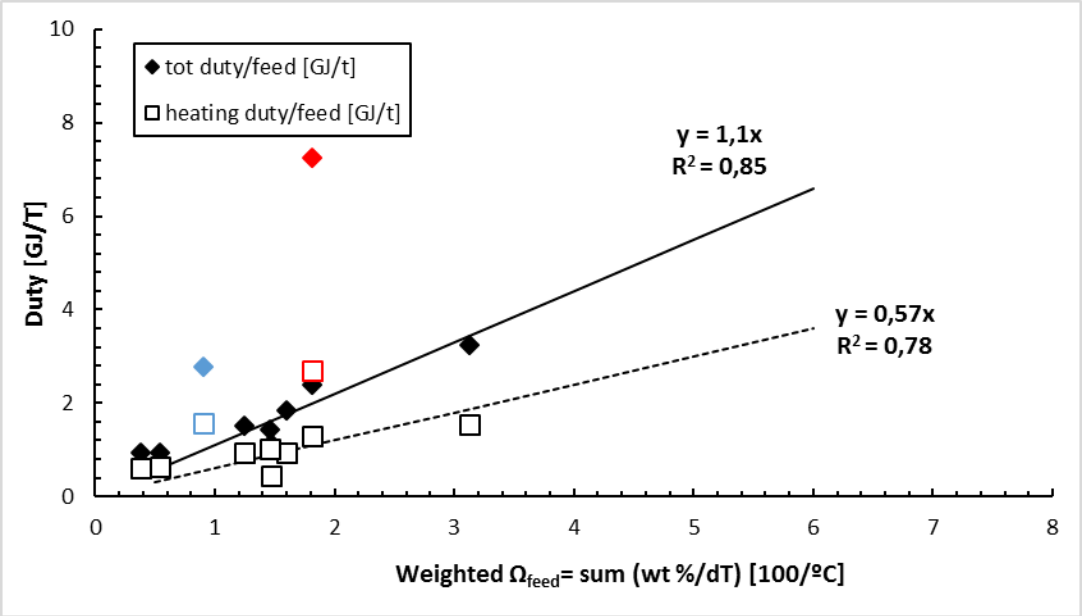

Figure 3.3 1st results without any correction applied for H_{vap} and compared to the correlation trendline for the distillation resistance of Jean Paul Lange [1], red points representing process 196 where large amounts of water are distilled and the blue points process 203 an unexplained outlier.

The 1st impression is that the majority of the ten distillation trains follow the proposed correlation. Very clear to see is an outlier, marked in red, that is far away from the usual points that are following the trendline proposed by J. P. Lange in his article[1].Furthermore, one other distillation train, marked in blue, also differs from the correlation. Both points are going to be analysed with more detail.

3.1.3 H_{vap} correction

From the figure shown prior the two outliers could be associated to their respective high H_{vap} values on a mass basis, having the red outlier, water, and the blue one, MeOH, distilled over the top of the column.

At this point of the research the idea came up that the best option could be to always use the H_{vap} correction factor shown in equation 16, on page 19. To validate the idea, it was tested and resulted in the following results when compared to the deviations originated by not using the mentioned correction factor.

Table 3.1 Difference in absolute deviation by using the Hvap correction factor with the proportion of the different enthalpies or not using it

Process	without H_{vap}	with H_{vap}
163	0,1	0,2
184	0,4	0,7
187	0,4	0,6
189	0,5	0,8
193	0,5	1,1
196	5,2	0,6
199	0,2	3,3
201	0,2	0,3
203	1,8	1,2
207	0,1	1,2

Seen in the table are the absolute deviations easier compared in the following figure.

Total [GJ/t_{feed}]		
Process	**With Hvap**	
163		-0,1
184		-0,3
187		-0,2
189		-0,3
193		-0,6
196		4,6
199		-3,0
201		-0,1
203		0,7
207		-0,8
Improved	**2**	

Figure 3.4 Hvap correction, represent the result from subtracting column 2 – column 3 in the previous table to show if a significant improvement is obtained by always using the correction factor H_{vap}, (Green: Improvement > 0,5 GJ/t_{feed}, Yellow: values in between -0,5 < x < 0,5, Red: Deterioration of > 0,5 GJ/t_{feed})

As expected, process 196 and also process 203 are improved from the H_{vap} correction factor. Nevertheless, process 187 and 207 also have MeOH being distilled and don't show improvements. The high H_{vap} is a result of the strong interaction in between the hydrogen bonds that create higher energy needs for vaporization. For the case of water in process 196 this is definitely the case since 83% of the medium is rich in this compound making it more difficult to vaporize.

For the other 3 process with MeOH distillation, 187, 203 and 207, these amounts of the hydrogen bonding rich compounds are not as high with the biggest stream distilled being 28% in process 187. In this way no explanation can be provided regarding process 203.

3.1.1 Comparison with the correlation

After the correction for the H_{vap} for process 196 (Water distillation) and neglecting azeotrope influence the following results are obtained.

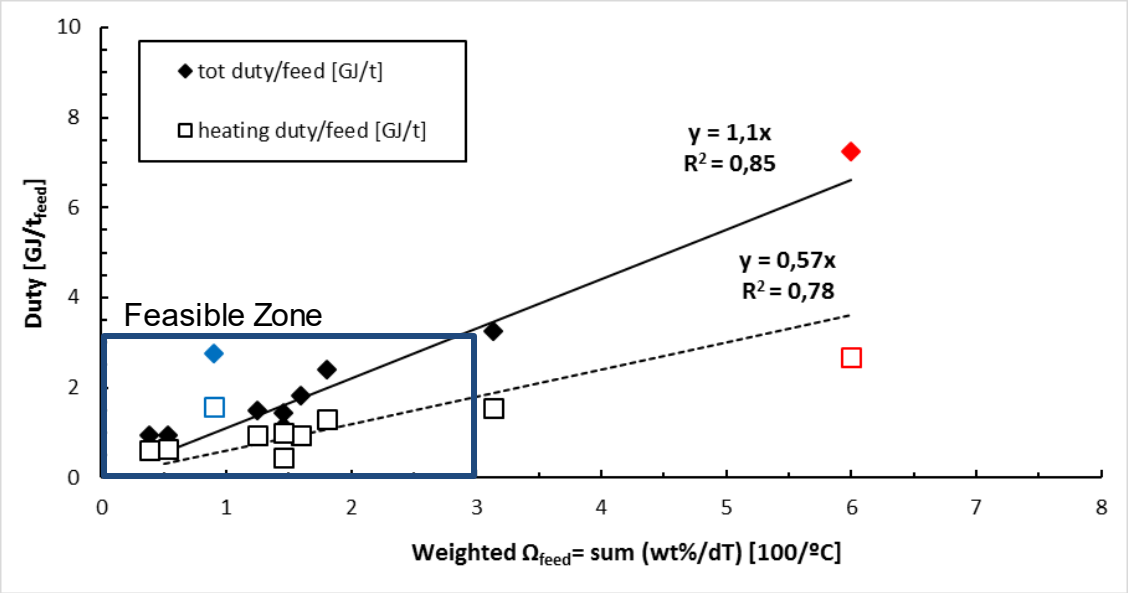

Figure 3.5 Final results of the distillation resistance calculations compared to the correlation of J. P. Lange[1] after Hvap correction and demonstration of the feasible zone inside which all the process should have any difficulty in separation)

The lines shown above are not the trendlines obtained, but the proposed correlation in the article of J. P. Lange[1]. Still the values are close with 1,15x for the total duty and 0,5x for the reboiler. It was opted to represent the graph this way to better validate the proposed correlation.

The standard deviation using the correlation for the PPD data set, ended up being much smaller than the one shown in the beginning for the distillation resistance equation. For the reboiler the distillation resistance deviated 0,51GJ/t_{feed} and for the total duty only 0,41 GJ/t_{feed}.

Resuming after the correction for the H_{vap}, all the points followed the proposed correlation, only process 203 still deviating more than the proposed standard deviation with 1 GJ/t_{feed}.
Goal of the distillation resistance was to see if a separation train is feasible. For this reason, the feasibility zone was established, around the 3 GJ/t_{feed} mark. All separation trains insight this zone shouldn't represent any major difficulties.

Also important was to identify what makes separation trains that fall outside of this zone needing so much duty for their separations. Looking closer at those process to see if a possible solution or substitution of the separation equipment or conditions can be made.

Ending outside the feasible zone could happen if there is one separation that makes the whole process needing more energy, a sum of medium to difficult separations or simply a very long separation train.

Looking at the dataset, the two processes that ended up outside the feasible zone were investigated, starting with process 199.

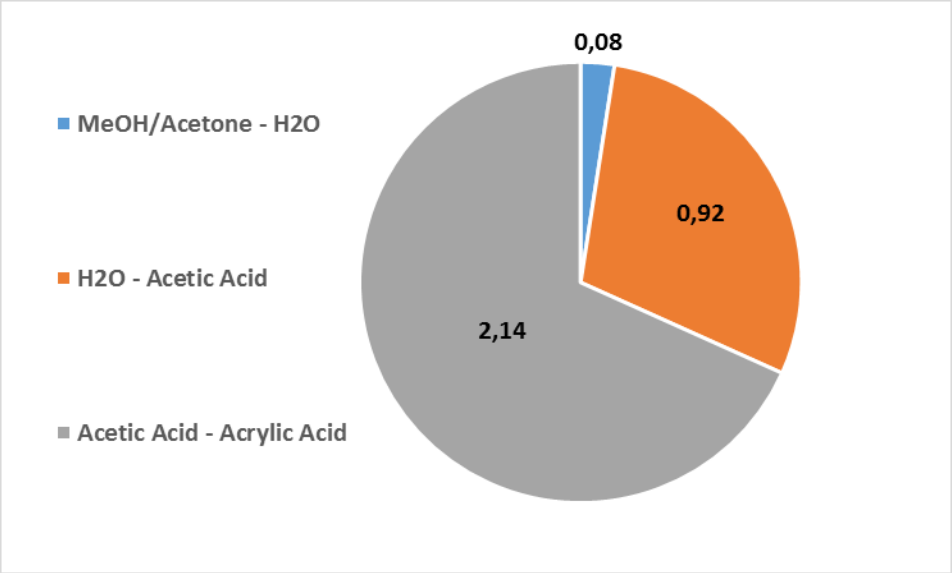

Figure 3.6 Breakdown of process 199 into its three sepearations happening along the distillation columns train expressed by its individual distillation resistance

Breaking down the separations of process 199 Acetic Acid to Acrylic Acid it becomes clear that separating the reactant, Acetic Acid, from the product, Acrylic Acid is costing a lot of money. The boiling point difference between these two compounds although not very small is part of the smallest with 23ºC. Furthermore, having 49% of the total inlet feed stream being Acetic Acid makes it a large flow to be separated over the top. After a short research no solution could be presented for this case.

Moving on to the second case the process 196 seen below.

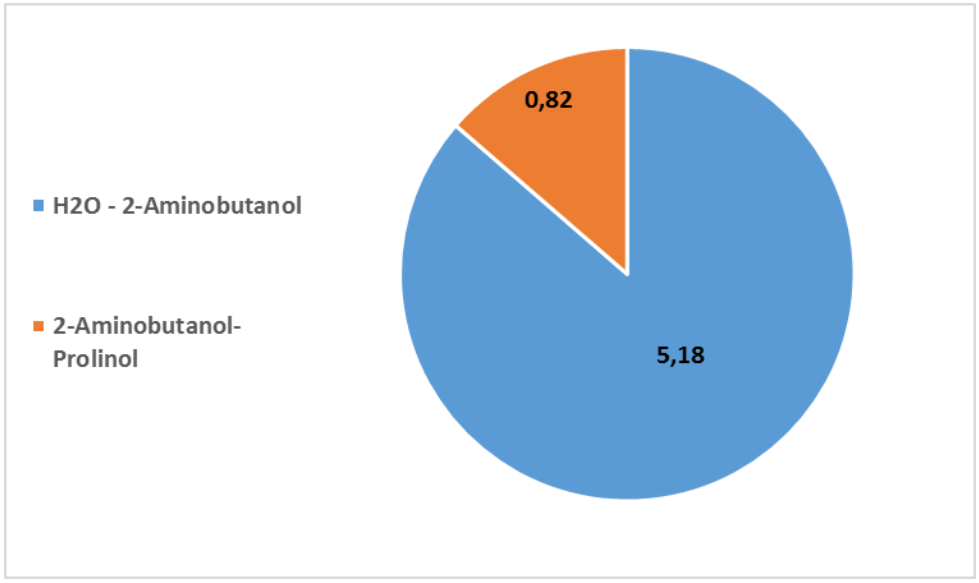

Figure 3.7 Breakdown of process 196 into its two sepearations happening along the distillation columns train expressed by its individual distillation resistance

Topping water from a distillation column, as seen here, is noy the best option for its associated high enthalpy of vaporization. The water present in this case used as solvent is existing in very high quantities. To be precise 83% of the total inlet feed stream consist of water that needs to be distilled. Although, as seen before, the raw materials are the major player for the profitability of a process, in this case the use of water and successive need to distill it adds a lot to the fact that this process is not viable at current market price conditions. In the PPD itself this question is addressed. The alternative proposed is the use of glycerol instead of water, option discarded due to the lack of known processes using this solvent.
More intensive research and pilot plants could show themselves to help to decrease these energy needs.

Some further results regarding influences of different variables, not as influential as the H_{vap} were also analyzed and are demonstrated in the following pages.

3.1.2 Azeotropes

The correlation is not set out for this mixtures being present in the distillation column as was said in the introduction. However, in two process azeotropes where distilled as a fraction. Taking the 1st case, looking at process 193 styrene and water form a low boiling point azeotrope. When no correction is made, the pure component boiling points are used and the average boiling point calculated for the separation the following results are obtained.

Table 3.2 Process 193 Calculations for azeotrope comparisons using the normal boiling points for average boiling point calculations in order to calculate the distillation resistance

Compounds	Feed %	NBP [ºC]	dT [ºC]	Ω_{feed}
Styrene + Water	92	138	65	1,4
MPK + MPC	6	203	164	0,0
DPEE	2	367		
Total	**100**			**1,5**

Resulting in the next table.

Table 3.3 Distillation Resistance process 193 for azeotrope comparisons using the normal boiling points, results and comparison with the *Unisim* data with the absolute deviation

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,4	0,9	0,4
Total (GJ/t_{feed})	1,1	1,6	0,5

The deviation obtained is perfectly within the deviation range of the correlation presented by J. P. Lange[1].

Comparing if now the azeotropic mixture is separated as one pseudo component, plus the styrene which is going to be in excess, an all of these are lumped in one fraction as showed for the calculations of an average boiling point the following results are obtained.

Table 3.4 Azeotropic conditions given by *Aspen* plus for water styrene azeotrope, molar,mass feed composition and its azeotropic boiling point

	Water	Styrene
Mol %	72%	28%
Mass %	31%	69%
NBP (ºC)	80,09	

Table 3.5 Lumped fraction (with the water styrene azeotrope) and the excess of styrene in order to calculate the distillation resistance

Pseudo compounds	**Feed wt%**	**NBP**
Azeotrope (Styrene + Water)	45	80
Styrene	47	145

If now the average boiling point calculations is applied;

Table 3.6 Process 193 Calculations of the distillation resistance applying the styrene water azeotrope with styrene excess as a fraction to be separated

Compounds	Feed wt %	NBP [ºC]	dT [ºC]	Ω_{feed}
Azeotrope (Styrene + Water) + Styrene	92	113	90	1,0
MPK + MPC	6	203	164	0,0
DPEE	2	367		
Total	**100**			**1,1**

Table 3.7 Process 193 distillation resistance results compared with the *Unisim* values when the styrene water azeotrope boiling point is used

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,4	0,6	0,2
Total (GJ/t_{feed})	1,1	1,2	0,0

Clearly an improvement is shown by using the azeotrope mixture values. The absolute deviation is reduced by half the size from what has been seen before.

Another case is process 163, the oldest PPD, in this case ethylene, benzene and water which all form an azeotropic mixture in between each other are separated as a fraction. Not using any azeotropic boiling points the correlation gives the following results for this case.

Table 3.8 Distillation resistance results 163, without any azeotropic correction

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,9	1,0	0,0
Total (GJ/t_{feed})	1,8	1,8	0,1

Seen that in this case three compounds form a azeotropic mixture in between themselves, lumping becomes more difficult and not so quickly. Looking at the results without any of the correction used, the deviation is still very small and well in the proposed range. In appendix E, page 70, a more detailed analysis is shown for this case.

For these two processes the estimated values fall inside the proposed standard deviation of the correlation.

Regarding if low/high boiling point azeotropes values could fix themselves at opposite limits of the correlation, as seen before in estimations of J. P. Lange regarding material costs[7]. In this case cheaper materials would end up on the lower limits of the equation and more expensive ones at the top.

3.1.3 Average boiling point

As approached and said in the introduction the average boiling point for a fraction was tested to confirm the use of the normal boiling point range calculations when confronted with fractions to be separated.

Another approach could be to use the boiling points of the limits, the highest boiling point of the fraction subtracted with the compound to separate underneath to obtain the temperature difference ΔT_{AB} and the lowest boiling point with the compound separated above for the same difference calculation. By comparing the two methods the following results showcased themselves.

Table 3.9 Absolute Deviations *Unisim*-Model comparing for the average boiling point for a fraction and when the limit boiling points of the fraction are used

Process	Average NBP	Fraction limit NBP
163	0,1	0,9
187	0,1	0,1
189	0,5	1,5
193	0,5	0,7
199	0,2	0,2
201	0,2	3,1

Subtracting the average boiling point calculated deviation from the other method, will indicate if using the boiling points from the limits of the fraction actually improves or not the outcome.

By not using NBP Range	
Process	**[GJ/t_{feed}]**
163	-0,9
187	0,0
189	-1,0
193	-0,2
199	0,0
201	-2,9
Improved	**0**

Figure 3.8 Improvement in GJ/tf_{eed} by not using the Boiling Point fraction equation (deviation Avg NBP – deviation limit of fractions NBP), yellow indicating no major improvement, red indicating a major deviation contribution

From this results it is clear to see that the average boiling point range is the best option to use, seen that none of the process was improved by using the other method. Especially for traditional refinery separations as seen in process 189 and 201, a different method as the one introduced in the first chapter brings large deviations with it.

3.1.4 Deviation trend

Finally, analyzing the trend Jean Paul Lange observed with the increase in the resistance compared to the research results. For his cases a clear rise in deviations appeared when the distillation resistance increased.

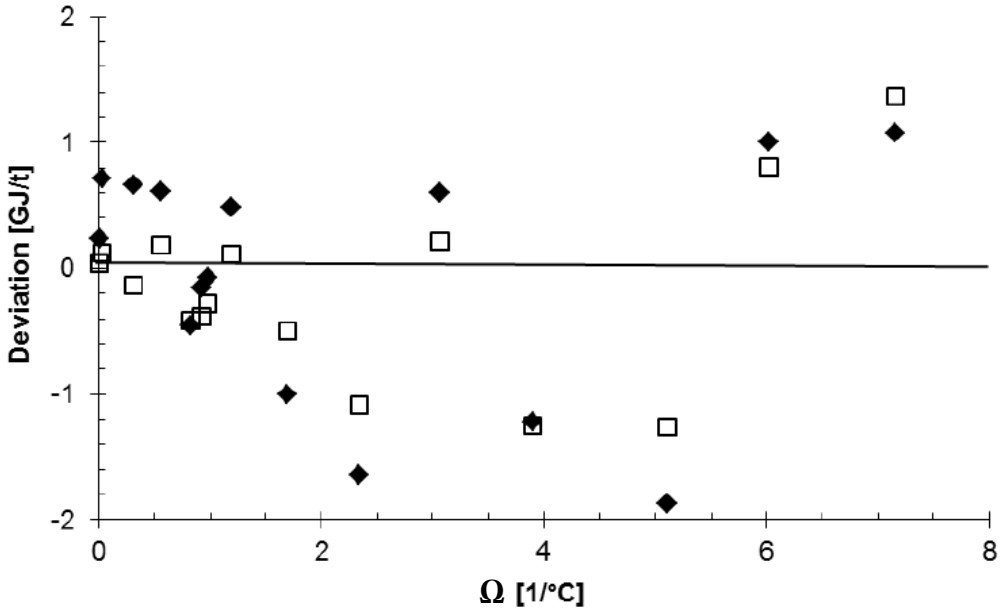

Figure 3.9 . Increase of deviation (*Unisim*-Correlation) with the increase of the distillation resistance[1] (1,1xΩ_{feed} for the total (fully black symbols) and 0.57 x Ω_{feed} for the reboiler (white squares))

For the data set analyzed this trend could not fully be confirmed, as seen below.

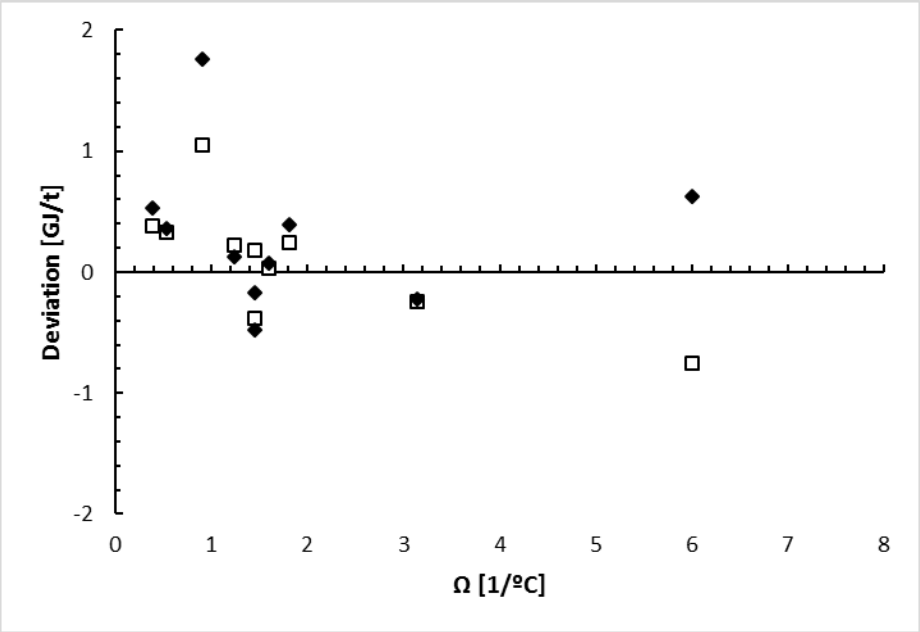

Figure 3.10 Same calculations as for the figure before (including already the correction for the H_{vap} for process 196)

It seems as no real trend can be seen. Still if process 203 the large outlier is taken out, a small similarity can be found in between the two figures.

Finally, one of the assumptions or better said conclusions for Jean Paul Lange's data was that the reboiler represented half of the total duty, this statement could be confirmed and is shown in appendix D, page 69.

3.2 Reaction Section – Duty

3.2.1 Final results - Reaction Section

The goal by adding this reaction section to the distillation section was to be able to have a full section duty estimation (heat exchangers + reactor). If required, the two parts could be analyzed separated to identify the energy consumers as seen for the distillation section with the separations happening inside the black box.

Looking at the parity plot exemplifying the duty estimation for the reaction sections larger deviations presented themselves when compared to the distillation section estimations.

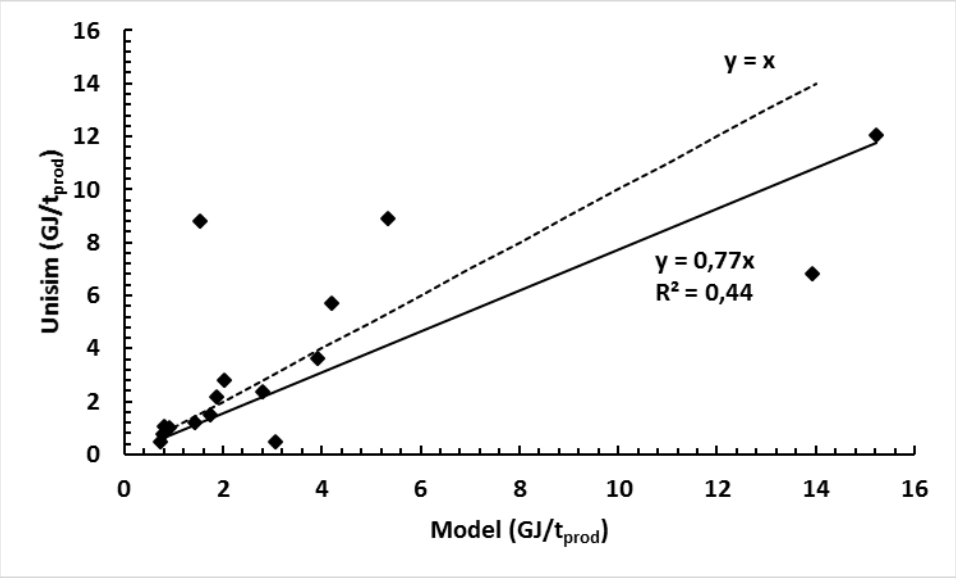

Figure 3.11 Parity plot reaction section (HE+Reactor), estimations using the equations presented and compared with the *Unisim* value, various outliers present with process sections 203-2, 203-1, 199-1, 187-2

Although from the graph it may not appear, with a standard deviation of 2.9 GJ/$t_{prod,}$ the correlation does not deviate much more, only 0,3 GJ/t_{prod} more than the one of the distillation column. The results in this case are strongly influenced by the heat exchanger estimations as its going to be seen in the following pages.

To have a better perception why this standard deviation may seem low when looking at the graph, the following figure helps to explain.

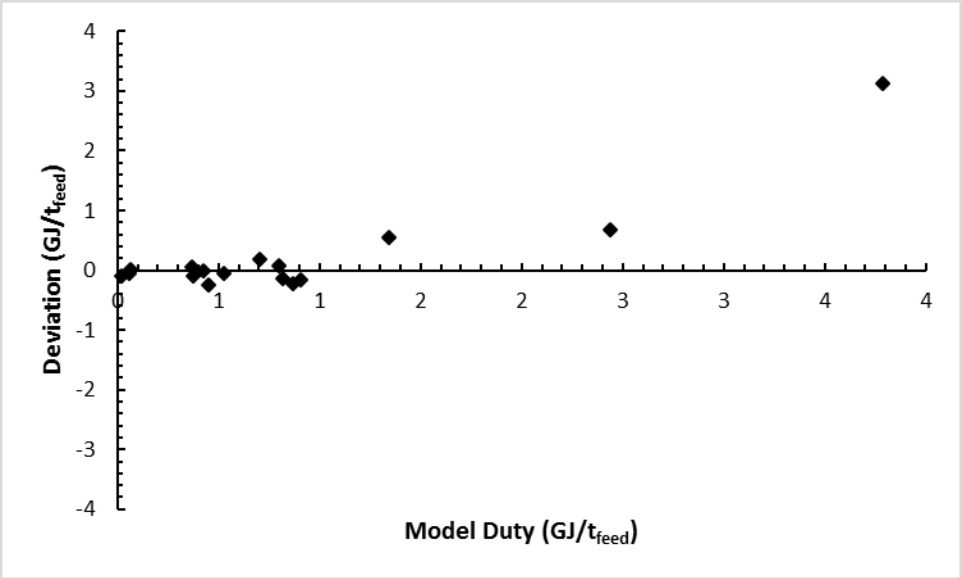

Figure 3.12 Deviation representing the difference of the (*unisim* duty – the model) in function of the model duty normalized per ton feed, representing the 2nd section of process 203 the large outlier

With this figure it gets easier to understand the mentioned low value of the deviation, this has to do with the high amount of points that are well estimated at lower duties. In this representation the duties are represented per t_{feed} to allow an easier comparison to the deviations presented for the distillation section and from the ones of J. P. Lange[1] at page 39 and the ones from the research at page 40 for the distillation section.
Clear to see is that for higher duties the deviations tends also to be higher, which was not seen so clearly for the distillation resistance for this data, but for J. P. Lange[1].

Showing the results for the reaction section estimation normalized per ton of product as what has been done before for the distillation section at page 30, the following can be seen.

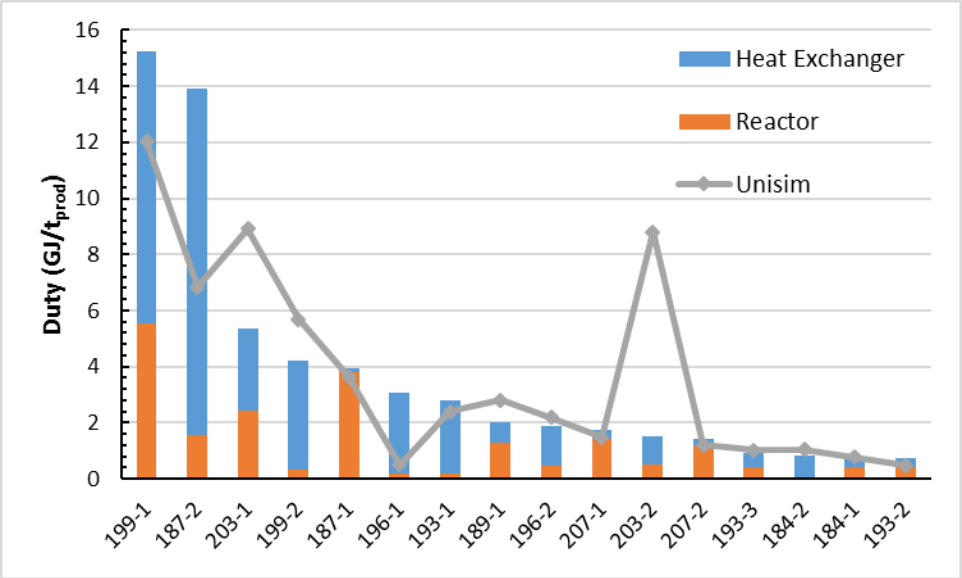

Figure 3.13 Estimation of duty (GJ/t_{prod}) for the reaction section and compared with *Unisim*, organized by energy demand and division in between reactor and heat exchangers

When compared with the distillation section the deviations are more frequent and also with higher magnitude. Nevertheless, the scales are different, since the duties for the distillation section are higher in value and with that may induce to a wrong interpretation of the size of the deviations. Also at this point no correction factors have been used, compared to the H_{vap} correction applied in the distillation section.

This figure beside showing the deviations gives a good indication on the distribution of the energy needs for each reaction section. As was seen in the distillation section it helps to identify the high energy consuming parts of the section.

Looking at the duty requirements, reactions of process 187 and process 199 show to be very duty needful. The larger peak, 199-1, has only 20 wt% of the reactants in the feed stream, also formaldehyde is produced by oxidation of methanol, which requires a lot of energy. Same goes for process 187, in this case propene is oxidized to propylene oxide.

The highest duty "allowed" at this point, for the reaction section, would be around 15 GJ/t_{prod} since it is known that process 199 is economically seen feasible. When this limit is compared with the distillation section which is around 11 GJ/t_{prod}, it is 4 GJ/t_{prod} higher. The value of the limit for the distillation section is from process 199, since process 196 with almost 40 GJ/t_{prod} is not feasible.

3.2.2 Reaction Section – Heat Exchangers

Having for all the processes a good estimation regarding quantity of heat exchangers inside the imaginary black box, is not an easy task. As mentioned in the introduction, page 10 and 11, three different approaches were tested and for the 16 sections the following results were obtained.

Table 3.10 Comparison heat-exchangers estimations in function of their absolute deviations for the reaction section using the different multiplication factors for their heating/cooling, H.I.= Heat Integration

	With H. I.	Dedicated Heater cooler	No H. I.
Factor	1	1,5	2
Lowest dev. (overall)	10	3	3
Lowest dev. (value)	0,03	0,06	0,14
Highest dev. (value)	5,5	11,7	17,9
Mean dev.	1,6	2,2	3,2

The initially proposed idea of the heating and cooling, the considered no heat integration, by multiplying the equation by a factor of 2 seems according to these results to have the highest deviation overall. The solution with a dedicated heater/cooler, using the factor of 1.5 instead of 2 improves the results already in a certain extend.

Still using a factor of 1, assuming heat integration, represents the best results, as is shown in the table and can also be seen in the subsequent figure.

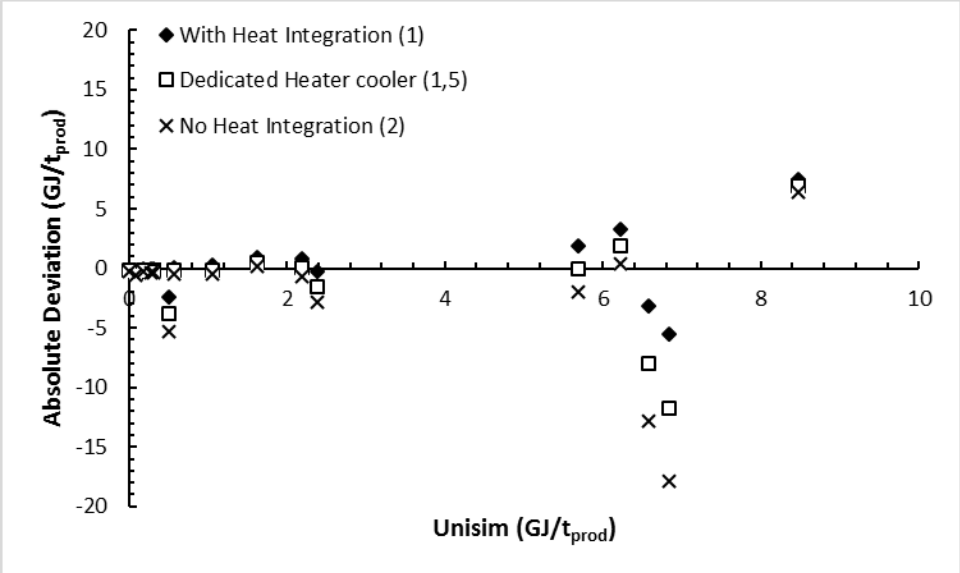

Figure 3.14 Comparison of the 3 different heat exchanger estimation coefficients and their absoulte deviations.

As said before the heat integration estimation results in most of the cases in more accurate estimations. From this point on all the calculations shown for the heat exchangers were calculated using factor 1 (heat integration). Representing the parity plot for the heat exchangers estimation the following figure is obtained, indicating the presence of deviations even with the correction of using the factor 1.

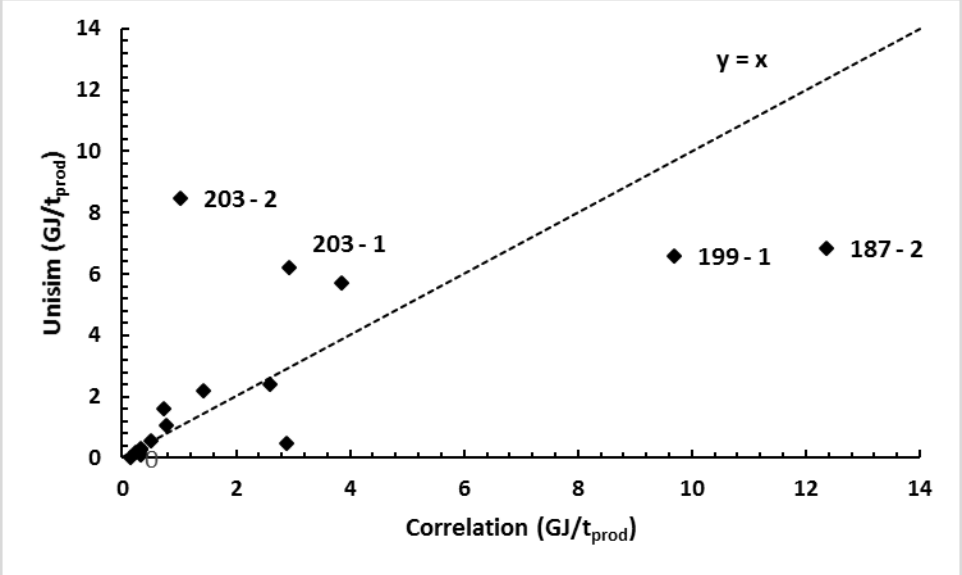

Figure 3.15 Reaction section - heat-exchanger estimations compared to their *Unisim* value with the parity plot, outliers indicated by process and section

The proposed assumptions for the use of this equation, shown on page 10, are not always fulfilled, as what was already expected regarding vaporization/condensation for example resulting in outliers. Still full association of deviations to the H_{vap} also cannot be made, since one of the outliers for example, deviated merely because the stream is heated up to 85ºC from 80ºC instead of the 30ºC. Another process deviates because only 5% of the total stream condensates after the reactor and no other heating or cooling is done.

In this initial phase the goal was to analyze if neglecting of this parameters could be done. From this results t is now clear that a very crude estimation is obtained which is not as accurate as what has been seen before.

The designer or user of this correlation should have in mind that although quick, the estimation for the heat exchangers will have this deviation associated for several reasons as mentioned.

Going back to the figure, looking at the biggest outliers, process 203 as seen already in the distillation section has a lot of water and methanol present, compounds that need more energy than others to either rise in temperature or to change its phase. In this case for the two outliers of

this process vaporization and condensations are present that may have altered the result when compared to the estimation.

Another case, for example the second reaction section in process 187 were only 5% of the feed stream cooled at the exit of its 2nd reactor, leading also to an overestimating of the model here.

A further breakdown can be found in the appendix F, page 74, regarding origins of the outliers for the heat exchanger estimations.

Trying to improve the method it was also tested if the estimation would give a better fit to just the heaters of the *Unisim* model since full heat integration is assumed for the calculations. If just the *Unisim* duties for the heaters were to be used, the designer would always integrate the cooler with the heater, ignoring the *Unisim* cooler afterwards in the final PPD report.
For the dataset only for one process a good improvement was achieved, but at the same time another one was deviated even further than previously.

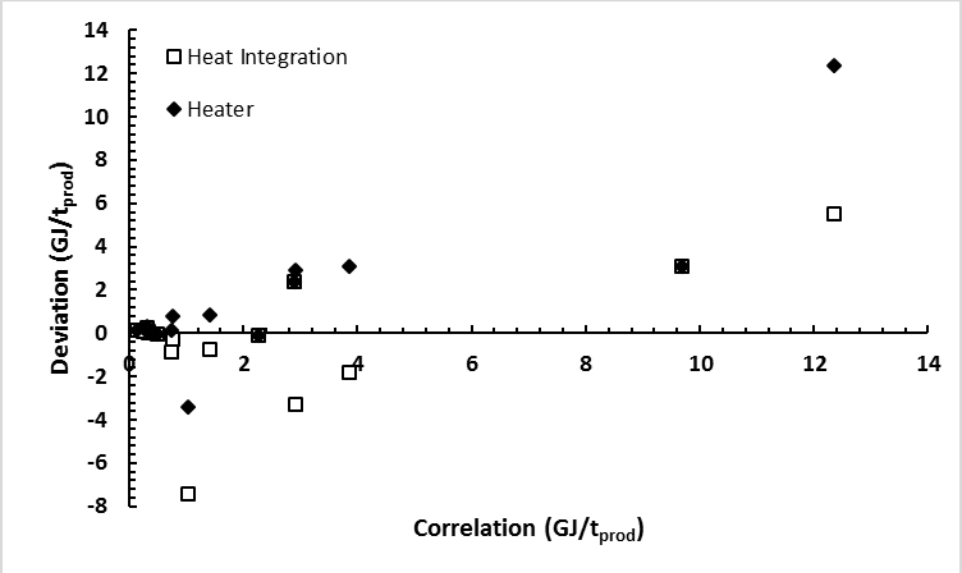

Figure 3.16 Comparing the estimation with the deviations of the Heat integration (Estimation - *Unisim* model of all HE) with the deviation for Heaters only (Estimation - *Unisim* (just Heaters))

As said before and can be observed no real improvement is obtained by just using the heaters of the *Unisim* model compared with the estimation method using factor 1 for heat integration.

3.2.3 Reaction Section – Reactor

For the reactor part, no real estimating is possible as sais previously, and with that no big deviations were noticed.

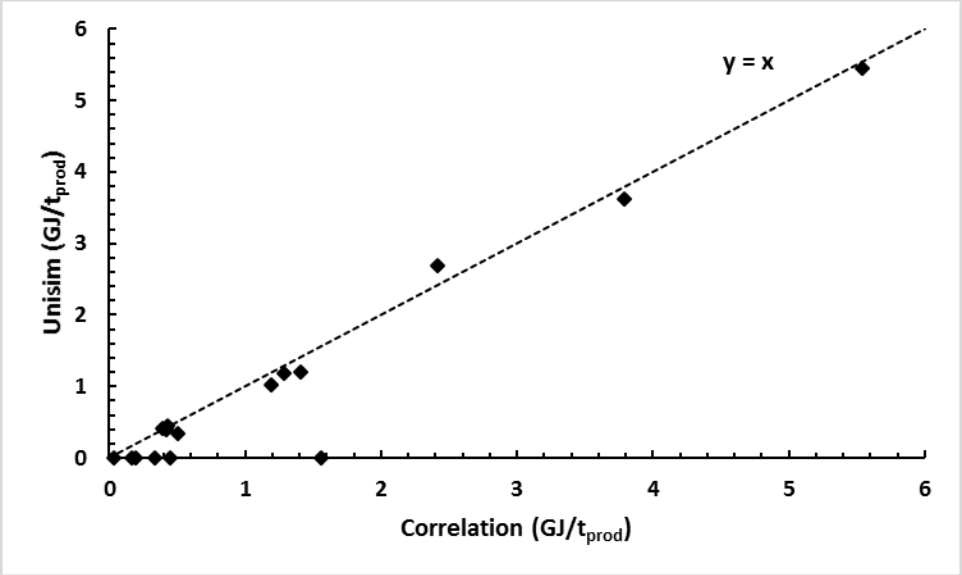

Figure 3.17 Reaction section comparison reactor estimation with *Unisim* estimations shown in the parity ploy

Some of *Unisim* data showed duties of zero for the reactors, this means that the designers opted to let the reactor operate adiabatically. This could be, for example, the case if the reactants are highly diluted in the mixture and with that the energy generated does not influence the whole reactor in a significant way.

Process 187, is exactly a case like that, in its second reactor the hydrogen peroxide that did not react in the previous reactor is decomposed for safety measures being in the inlet feed stream present at very low weight percentage. For this reason, the product mass created is very small compared to the total stream with only 0.81 weight percentage, meaning that the temperature change is being controlled just with the mixture it is diluted in.

In three of five processes where no heat is transferred in the reactors according to the simulation, a positive deviation is present in the heat exchanger, indicating that the energy that is not being used to control the reactor is being applied here. However, this trend only represents 60% of all the processes where this is the case and in this way the idea that for adiabatically run reactors the heat is compensated in the heat exchangers cannot be confirmed.

From all the process the major energy consumers are exothermic reactions, being 207-1 the 1st endothermic reaction shown in the figure with an estimated value of 1.2 GJ/t$_{prod}$.

3.3 Cost estimation

3.3.1 Ω_{prod}

Moving on to the costs, in order to know if the proposed distillation cost limit of 100\$/t_{prod} is fulfilled and also if this value goes well with other processes the following table was elaborated for the PPD's.

Table 3.11 Data for the Ωprod calculations in order to check the prohibitive limit of 100\$/t, including weight percentage of sellable product, capacity of the plant, calculation for the cost using equation 10, page 9.

	163	**184**	**187**	**189**	**193**	**196**	**199**	**201**	**203**	**207**
Ω_{feed}	1,6	0,5	1,3	0,4	1,5	6,0	3,1	1,5	0,9	1,2
Wt % Prod	28%	18%	16%	100%	79%	17%	31%	100%	58%	23%
Price ($ 2003)	\$887	\$994	\$1 588	\$756	\$1 221	\$1 396	\$1 052	\$239	\$495	\$491
Ω_{prod} (100/ºC)	5,7	3,0	8,0	0,4	1,9	35,3	10,1	1,5	1,6	5,4
Capacity (kt/a)	600	33,6	300	668	600	25	200	798	179,2	450
Distillation Cost ($2003/t)	36,9	44,7	55,6	4,5	15,1	303,1	72,6	11,7	17,7	37,4

Process 189 and 201 are typical refinery process and for that reason have 100% product. The tables result in the subsequent figure.

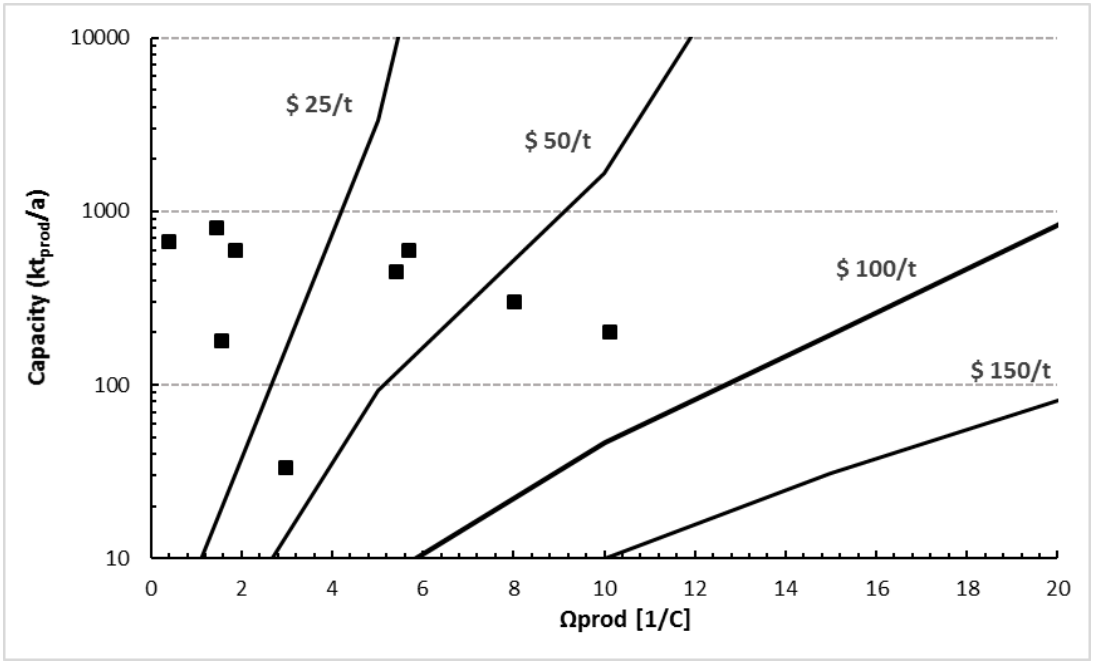

Figure 3.18 Distillation Cost in order to check the prohibite limit of 100\$/t (process 196 not included for having a cost of 303 \$/t), second largest point is process 199

Visible in the figure, the distillation cost limit from Jean Paul Lange is not reached for almost all the PPD's. Process 196 was excluded from this figure since its distillation costs, as could be foreseen from the prior results, is prohibitive with 303 $\$/t_{prod}$ shown in table 3.11. The most unappealing process, after 196, is exactly the 2nd one pointed out in the distillation resistance, process 199. Process 187 which for the GJ/t_{prod} was 2nd in duty consumption actually ends up having a low distillation costs due to a higher capacity, 50% larger than process 199. This is a good example of the effect of the economy of scale for two process that at the origin were similar in difficulty with 199 and 187.

Since no specific OpEx costs could be extracted from the PPD no comparisons were done for this correlation.

3.3.2 Distillation Section - CapEx

Looking at the CapEx calculations for the distillation section the fact that equation 3 on page 4, largely overestimated the ISBL costs were observed. Nevertheless, it was possible to see that the PPD´s actually followed a similar trend line, just with a lower multiplication factor.

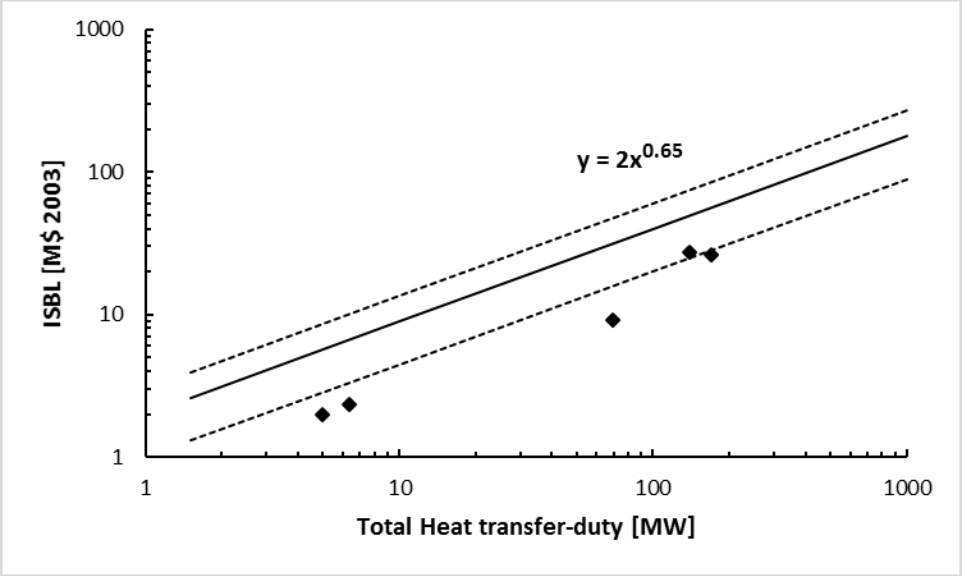

Figure 3.19 ISBL in function of the Total Heat-transfer duty of *Unisim* [MW] compared with J. P. Lange correlation (dotted lines -50% and +100% if the equation)[1]

All the points end up on top of the -50% dotted line. Even the two processes that show to have duties under the critical 10 MW value referred on page 4, do not seem to fall outside the trend.

Correlating with the distillation resistance, equation 7, page 8, should enable the calculation of the ISBL using only the feed rate and the distillation resistance.

It must be mentioned that the proposed factor of 0.24 is not from historical data but from a conversion calculation, demonstrated in the appendix A, page 65.

When the historical points of J. P. Lange were plotted in function of the ISBL, the equations multiplication factor for the trendline, approached the value with a very similar number 0.2168 instead of the 0.24 in his paper as can be seen below.

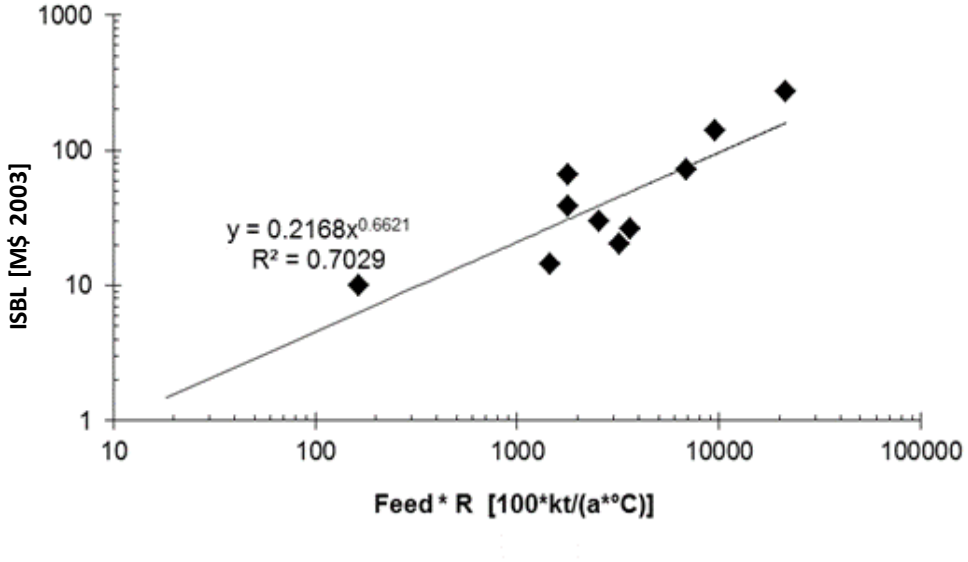

Figure 3.20 J. P. Lange correlation of the historical duty data with the ISBL costs, giving a similar multiplication factor as the proposed 0,24

For this research all the processes fall short in value and show themselves to be very cheap. Sometimes the costs present to be even more than half the price of the correlations results.

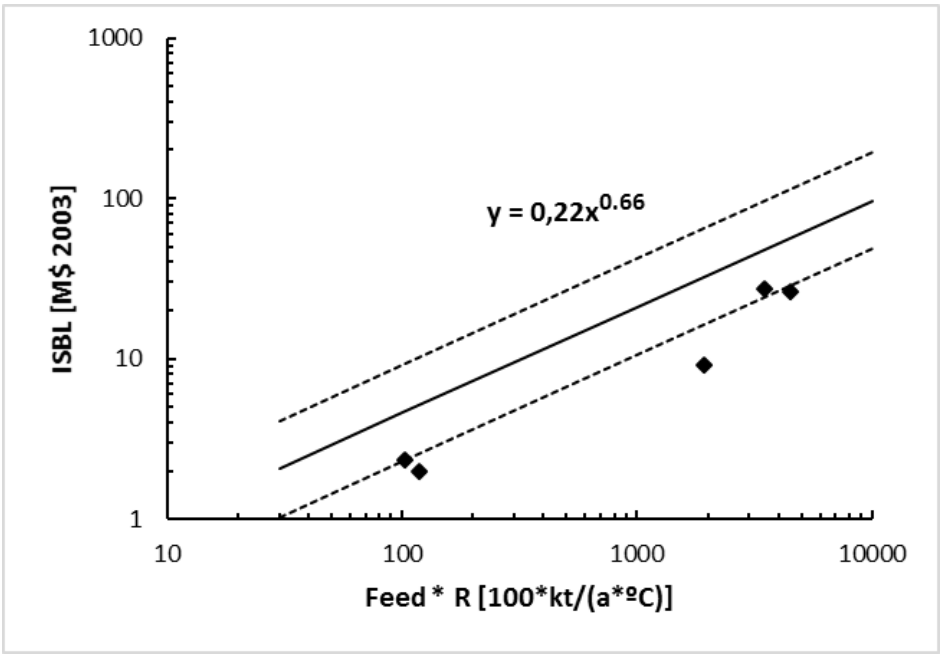

Figure 3.21 . Correlation of equation 7, page 8, to obtain the CapEx (ISBL), using the multiplication factor of J. P. Lange historical data trendline and with the -50% and +100% lines plotted

As can be seen the the points follow the same line as seen before, but end up on the lower part of it, confirming the same trend seen when the *Unisim* estimations were plotted against the investment costs. The difference here is that the values of the duty are estimated through the distillation resistance as said before to have the result quicker. The reason could be due to the *ISBL* conversion factors used, also another reason could be that the process from *Shell* which some are already almost 20 years old have values that end up being difficult to compare to these more modern processes. Looking at the conversion factors, converting the costs of the equipment by a factor also including *OSBL*, as seen in some reports, to obtain the total installed costs with a factor of 6.3, instead of Lang's 4.74 improves the accuracy.

3.4 Reaction Section - CapEx

In general, for the reaction section the majority of the CapEx values fell inside the correlation's limit. If the CapEx values are represented in function of the *Unisim* duties to compare to the correlation of equation 3 on page 4, including reactor and heat exchangers, the subsequent figure is obtained.

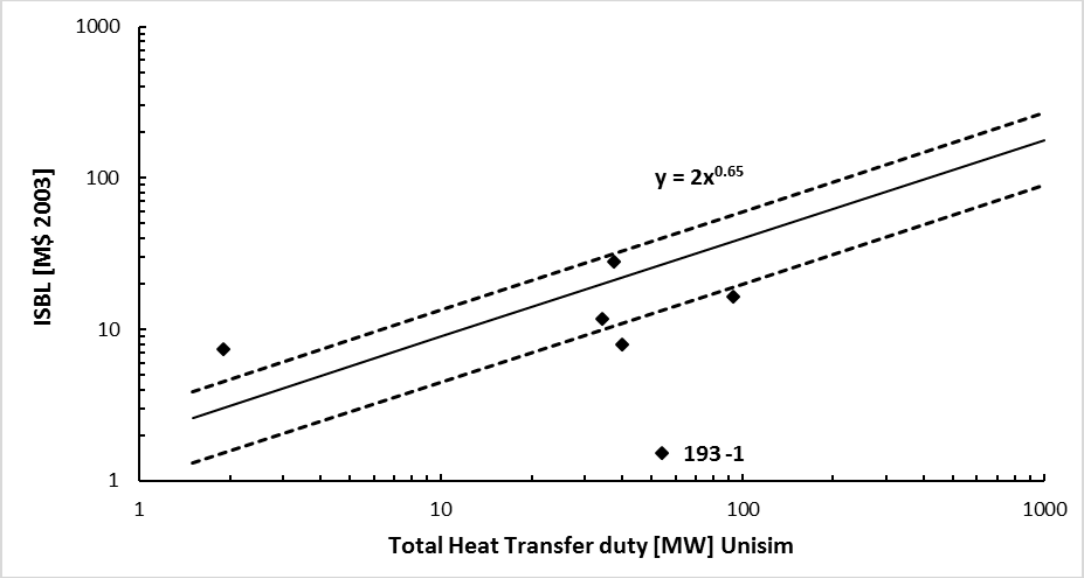

Figure 3.22 CapEx Reaction section (reaction section 187-2 (2 MW;0,6 M$), 193-2 (11 MW;0,7 M$), 193-3 (19 MW; 0,4 M$) and 196-1 (0,5 MW; 2,3 M$) are not included for not being possible to represent on the log scale, reference lines used from J. P. Lange[6]

As pronounced in fuels and chemicals manufacturing the costs for the reactor section duties tend to be higher[4], this statement is observed for at least two values with the second section of process sectio196 and the first of PPD 187.

Interesting to see is that the second reaction section of process 196 also seems to represent the same deviation as seen in J. P. Lange's data for processes under 10 MW[1], which was not the case

for the distillation section values. Some processes have lower transfer duties or CapEx values than one and are reported in the caption. The first reaction section of process 193, at the bottom outside of the correlation scope, represents an acylation reaction to produce M-PH-Ketone from Benzene and Acetic Acid in an adiabatic fluidized bed.

Not only the reactor type is important but as well the heat exchangers seen that these costs are also included in the section. For example, in this case almost all the duty in the section comes from the heat exchangers, giving an indication that maybe the correlation estimates better the costs if the duty is all in the reactor or at least the majority of it. An analysis for this trend can be seen in appendix G, page 78. For process 193 the values are all underestimated, since the other two sections, although their duties are over 1 MW, are not even in figure for being too cheap, showing that this could be a special case.

When the duties for the reaction section are estimated, instead of using the *Unisim* values, the points stay for the majority of cases inside the boundaries as well. The 1st reaction section of process 196 is also present in the next figure as it is overestimated by the correlation.

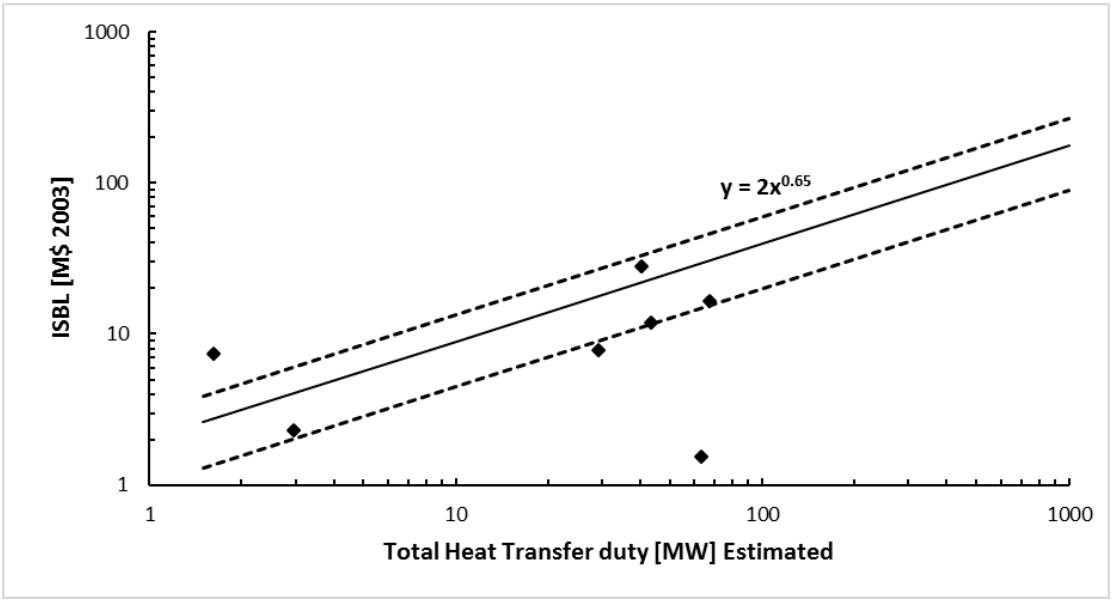

Figure 3.23 CapEx Reaction Section (Estimated), (reaction section 187-2 (2 MW;0,6 M$), 193-2 (11 MW;0,7 M$), 193-3 (19 MW; 0,4 M$) for not being possible to represent on the log scale, reference lines used from J. P. Lange[1]

Here again the same results can be observed as already previously that all the processes represented end up inside the dotted lines beside the first section of process 193. Also the second reaction section of process 196 follows the trend observed for values under 10 MW. The first reaction section of process 196 present, also ends up inside the boundaries although its energy demand is under 10 MW.

3.5 Adding Sections - duty

At this point a first glance can be given how adding the two sections, distillation and reaction (HE + reactor) could look like. To do this the reaction sections for each process were added up in order to give an indication of the percentage they represent of the total duty of the process. This way a clearer idea can be given of which type of sections are the big energy consumers. The parity plot for the sum of the sections (reaction + distillation) gives more clear guidance on the exactitude of the method on a global basis.

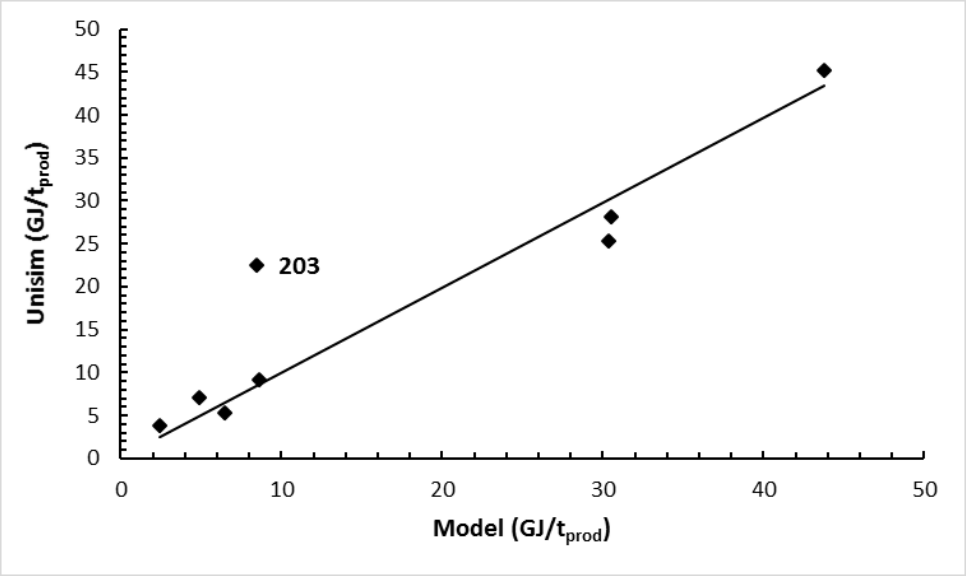

Figure 3.24 Parity plot two sections added up (duty section + reaction section (reactor + HE)) compared with the Unisim estimations, having only 203 as unexplained outlier

It is very interesting and good to see how accurate and good the estimation ended up being when the sections were summed up. PPD 203 being the largest outlier probably due to the compounds present in the streams with different Cp's and H_{vap}. The parity plot for each section either distillation or reaction individually, presented underneath, shows just a mere conclusion of the whole research with lower deviations for the distillation resistance obtained duties.

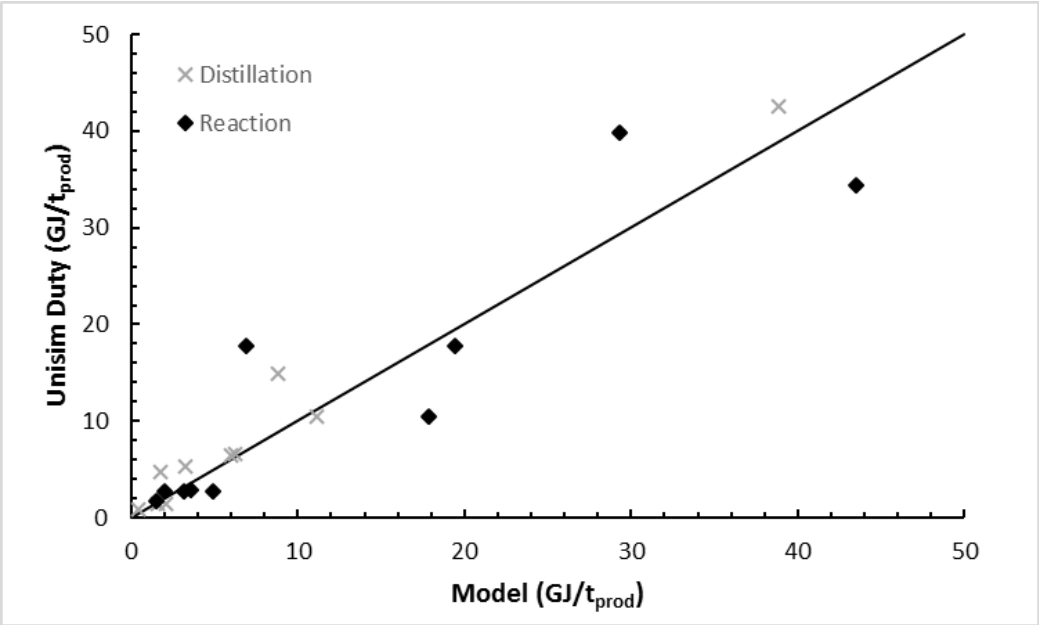

Figure 3.25 Parity Plot estimations of distillation section and reaction section individually compared to the Unisim values

The majority of the points end up in the small scatter at the bottom left of the figure indicating an easy separation or reaction. The values inside this scatter are difficult to estimate since the standard deviation of 4.7 represents almost the entire number of the duty, similar to what had been seen for the feasible zone of the distillation resistance where the points that end up inside are difficult to predict with accuracy.

Analysing the duty for each process by its individual sections.

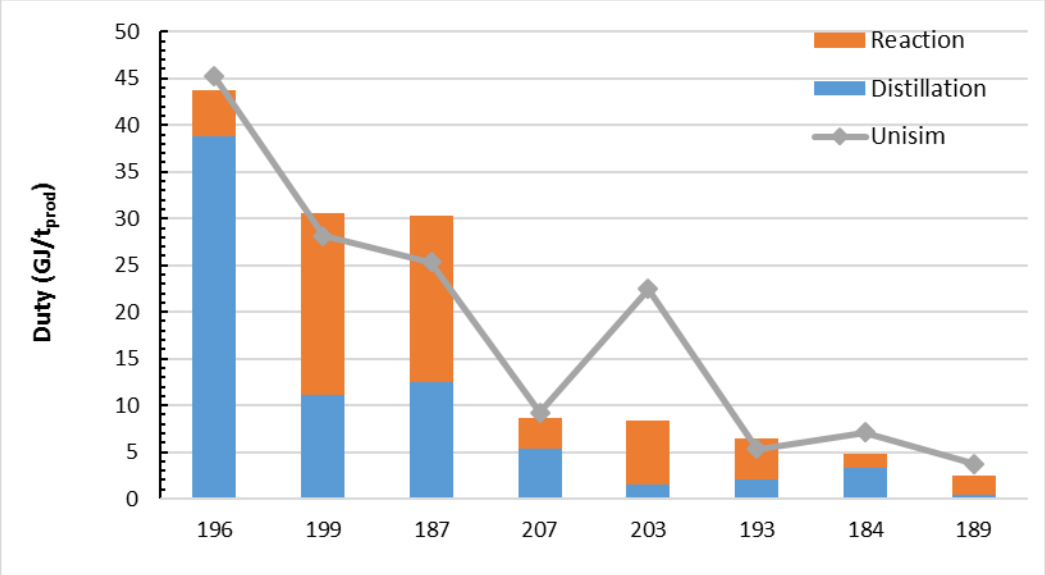

Figure 3.26 Reaction (HE + reactor) and distillation section summed up and compared to the *Unisim* data, organized by duty requirements and different section parts (distillation/reaction)

Process 187 and 203 still show the same trend for deviation, specially 203 having over 200% of its own value overestimated due to its high heat exchanger estimation deviation, as well as the deviation originated in the distillation section. After adding the reaction sections PPD 199 gets more accurate due to an overestimate on one section and an underestimation on the other.

Discussed already in the distillation resistance process 196 shows an overall strong need for duty for its separation train, when compared with the others that show a better balance in between the sections. This also shows the impact that a solvent, used in this process, can have on the total duty of a process. For case 196 almost over 85% of all the duty is needed just to distil water, reminding that the right method to separate or the reaction chosen for each section needs to be selected with caution. Reinforcing the importance of the distillation section when compared with the reaction section for the feasibility of a project.

3.6 Adding Sections – Cost Estimation (CapEx)

Finally analysing the CapEx estimations for each of the sections and in between them the following figure is obtained.

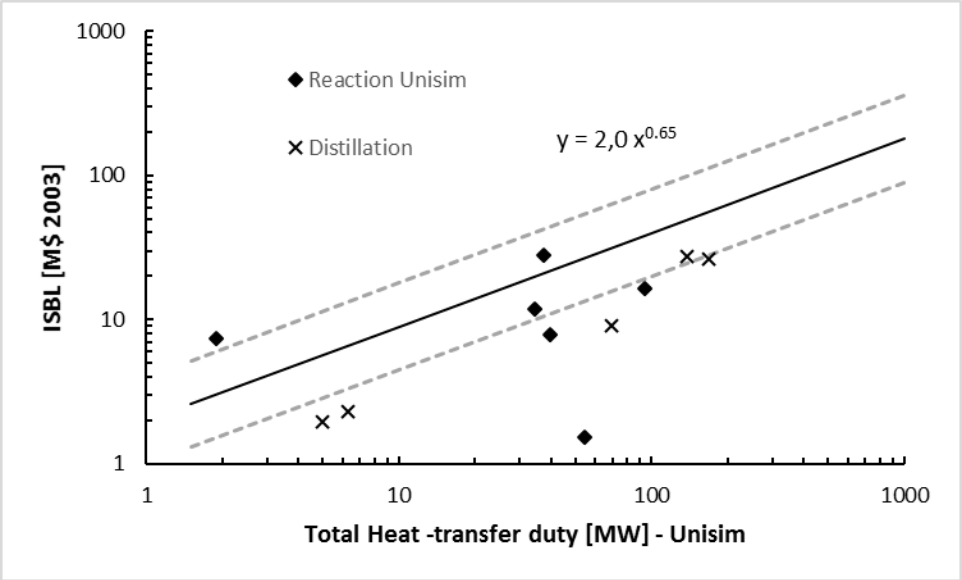

Figure 3.27 ISBL for each section,), (reaction section 187-2 (2 MW;0,6 M$), 193-2 (11 MW;0,7 M$), 193-3 (19 MW; 0,4 M$) for not being possible to represent on the log scale are not shown, reference lines used from J. P. Lange[1]

This figure resuming all the previous shown data demonstrates what already had been seen, that in general lower values of the distillation section estimations are obtained when compared with the reaction section, going in line with the interpretation of J. P. Lange [4]. Still, beside the lower investment value for process 193, the correlation in its full scope can give, with a certain margin of 50% to 100% with M$ 2003 scale, a good estimation of the ISBL CapEx price.

4 Conclusion

Concluding, the distillation resistance gives a good and quick analysis of the difficulty of a separation. Furthermore, making it easy to find what is hindering the train to be less energy needful by identifying which separation of the train has the highest consume.
The feasible zone is a good validation for doable separations and all the points outside should be closely reviewed.
Processes with high amounts of MeOH or Water need more attention because not using the H_{vap} correction factor can decrease the estimations accuracy a lot, up to eight times. Values where 83 wt% of these two compounds are to be distilled should be treated with attention. In the range in between 25% until 83% the mind-set should be that at some point a tipping point will arrive where applying a correction factor will be crucial.
Although more validation should be performed the results indicate that the distillation resistance can give a quick valid duty estimation, deviating only around 0,51 GJ/t_{feed} in this analysis for the reboiler and even less for the total duty with 0,45 GJ/t_{feed}. For the points inside the feasible zone this standard deviation can still be at some point to high compared to their own values and attention needs to be taken.
To summarize, it can be used as a short cut for duty estimations improving the long-time spend to obtain results, although with a certain deviation associated.

Advancing to the Ω_{prod}, the distillation resistance in function of the product, it provides an interesting look of the resistance by showing how efficient a process is. The proposed limit of J. P. Lange of 100 \$/t[1] can be an indication but should not be held as total reference as no price of product or gross margin is taking into account, although for this research it showed to be right. For example, a process could have a distillation cost over 100 \$/t but still be viable if for example the gross margin, the major influence on profitability, as well as market demand for the product, allows it to be. Further research on this specific topic could give better guidance.

The reaction section although not investigated with the same extend ended up giving some interesting results, furthermore allowing a more complete view of the process.
Main conclusion here for the duty estimation is that the heat exchangers dominate the outcome of the results in terms of accuracy. Whether it is the amount of units that heat or cool a stream, the compounds with different Cp´s than 2 kJ/kg.ºC or phase changes, all or some of them affect the end outcome a lot. Eventually deviations can go up even over 100% of the *Unisim* value itself, being the highest value 7,4 GJ/t_{prod}

For the reactor duty estimation, as previewed, no mentioning worth deviation occurred, being the only step back the more time consuming calculations when compared to the other estimations.
From the results and figures as done for the distillation resistance a good focus can also be made on where the high duty is needed and what could be the cause.
This closer analysis goes in line of what is already desired for the distillation resistance, a guidance of where the biggest resistance, this case where the highest energy consumer is.
Concluding the reaction section, concerning its duty forecast it still needs more research to have more uniform results as seen for the distillation resistance. Nevertheless, the deviations obtained for the parity plot just for the reaction section is not much higher than the one for the distillation resistance. It is clear to see that for the reaction section a lot of points with higher values tend to get away from the proposed correlation, attention needs to be taken for these situations. It can be concluded that with not a large deviation a good indication can also be given for the final duties that could be involved, yet some larger deviations may present themselves when compared with the distillation resistance.

By adding up the sections for their duty estimations a better global view of the process is gained and conclusions can be made upon the more difficult aspects of an almost complete process. This way quickly the highest global energy consumer can be identified and zoomed in to discover the reason.

Looking at the costs, the CapEx values ended up giving good estimations for the small data set at hand. The majority of points fell under the 10 MW and some also under the 1 MW mark making it more difficult to obtain a good validation. Still for all the process sections shown it could be concluded that the distillation sections tended to be cheaper than the reactor sections. The costs for a process section can be estimated using the correlation, with the values being inside the scope of -50% and 100%. However, this estimation must be seen as a crude one, since the values are represented in a log scale and in M$ 2003 making deviations go up to several million dollars.
Overall the estimations presented in this research can give quick good duty estimations, needing definitely improvement for the heat exchangers.
Concerning CapEx values crude estimations can be obtained but shouldn't be used with certainty. Interesting to point out is that equation 2, page 4, has been used successfully by recent independent research with similar results[8] and [9].

The quickness of results and the simplicity in calculations make these correlations an interesting addition to the feasibility analysis of a process by boosting the time won through its quick duty estimation.

5 Recommendations

Concerning the duty estimation for the distillation section important to discover would be the limits of wt% of Water and MeOH before the correction factor needs to be used.
Also for the distillation resistance duty estimation a closer look and extension in the use of azeotropic mixture would be interesting to find out if a correction needs to be made or if the values always end up inside the standard deviation for the equation.

The biggest interest and improvements can be achieved for the heat exchanger estimation in the reaction section. Confirming the limits of the Black Box, the confirmation of the factor 1, assuming heat integration, Cp influence and also phase changes would definitely upgrade the outcome and clarify sensibility of the result for each of the mentioned variables.

Adding to this, having a similar resistance to be used for an extraction column could add another section to estimating the whole process, furthermore it could be well integrated with the distillation column if it is set to recover a solvent for example. The approach could be a similar one as with the distillation resistance, being here the driving force the interaction in between solvent and solute, as compared with the boiling points for the distillation columns. This could make for a resistance that would be in a similar range as Ω_{feed} making it also possible to estimate the costs: how much solvent (OpEx) or how expensive the column could/would be (CapEx).

Having more processes analyzed concerning their CapEx values would validate the proposed equation, especially looking at the distillation columns as it is not clear if the data of J. P. Lange[1] included also heat exchangers or not.

Finally, with net margins for the revenue and the raw materials, maybe a limit could be imposed for the rest of the process duty requirements to still be feasible. This could add an interesting factor to the estimation as the duties could be seen in correlation to this imposed limit from the raw profit. This limit could have been used to compare the three high duty requirements of processes 187, 196 and 199. For example, from the PPD´s it is known that 187 and 196 are not viable, but 199 shortly underneath is. A possible limit could have shown this conclusion even without the need of the time consumed to arrive at this closing with the whole flowsheeting.

6 Bibliography

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7 Appendix

7.1 Appendix A – Investment conversion calculations from historical data

In order to be able to estimate the investment cost directly from the distillation resistance feed the following conversions had to be done.

Knowing that

$$Investment\ (ISBL)\ Section\ [M\ \$\ 2003] = 2.0 \times (total\ duty\ [MW])^{0.65} \quad (20)$$

And

$$total\ duty\ [MW] = total\ duty\ \frac{[\frac{GJ}{h}]}{3.6} \quad (21)$$

Assuming 8000 h production hours per year (annum):

$$feed\ \left(\frac{t_{feed}}{h}\right) = feed\ \frac{\left(\frac{t_{feed}}{h}\right)}{8000(\frac{h}{a})} \times 1000\ (kt_{feed}/t_{feed}) = \frac{feed\ \left(\frac{kt_{feed}}{a}\right)}{8} \quad (22)$$

and that

$$total\ duty\ (\frac{GJ}{t_{feed}}) =\ 1{,}1\ \Omega_{feed} \quad (23)$$

Results in in adding all the equations,

$$2\ x\ ((\frac{1{,}1}{3{,}6*8})feed\left[\frac{kt}{a}\right] x\ \Omega_{feed}))^{0.65}\ = 0.24\ x\ (feed\left[\frac{kt}{a}\right] x\ \Omega_{feed})^{0.65} \quad (24)$$

Combining the equations allows us to quickly estimate the cost based on the distillation resistance feed as seen below:

$$Investment\ (ISBL)\ Section\ [M\$\ 2003] = 0.24\ x\ (feed\left[\frac{kt}{a}\right] x\ \Omega_{feed})^{0.65} \quad (25)$$

7.2 Appendix B - Distillation Cost Calculations

7.2.1 Calculating the distillation cost based on J. P. Lange's article[1]

Extracted from the paper of J. P. Lange the following calculations are presented to get to the distillation cost which is in fact a sum of the operating and capital expenses.

$$Distillation\ Cost\ \left[\frac{\$\ 2003}{t_{prod}}\right] = OpEx\ \left[\$\frac{2003}{t_{prod}}\right] + CapEx\ \left[\$\frac{2003}{t_{prod}}\right] \quad (26)$$

For the CapEx estimation the final equation is obtained as followed.

$$CapEx\ \left[\frac{\$\ 2003}{t_{prod}}\right] = CapEx\ [M\$\ 2003]\ x\ 0.25/Product[\frac{Mt}{a}] \quad (27)$$

Assuming 25% capital charges [6].

$$CapEx = 0.24x(Product\ \left[\frac{kt}{a}\right] x\Omega_{prod})^{0.65}\ x\ 0.25\ x\ 1000/Product[\frac{kt}{a}] \quad (28)$$

$$CapEx\ [M\$\ 2003] = 60 \times {\Omega_{prod}}^{0.65}/Product^{0.35}[\frac{kt}{a}] \quad (29)$$

The OpEx value can be approximated using the heating duty as a variable and multiplying it by an average market price of 5 [$/GJ] for the energy needs.

$$OpEx\ \left[\frac{\$}{t_{feed}}\right] =\ 5\ \left[\frac{\$}{GJ}\right] \times Firing\ Duty\ \left[\frac{GJ}{t_{feed}}\right] = 2{,}85\ \Omega_{feed} \approx 3\ \Omega_{feed} \quad (30)$$

Adding the two contributions the distillation cost can be calculated quickly using the following equation

$$Distillation\ cost\ \left[\frac{\$2003}{t_{prod}}\right] = \left(\frac{60 \times {\Omega_{prod}}^{0.65}}{Capacity\ \left[\frac{kt}{a_{prod}}\right]}\right) + 3 \times \Omega_{prod} \quad (31)$$

7.2.2 Fixing the distillation cost

To obtain and compare the distillation cost graph from J. P. Lange figure 1.5, page 11, the distillation cost had to be fixed at a certain value. Using differente distillarion resistance of the product as a variable and giving various results in capacity in kt/a the lines for the graph could be drawn. The tables following are the results of the calculations.

Table 7.1 Fixing the distillation cost at 25$/t to obtain the distillation cost line in function of the $\Omega_{prod,}$ x= $\Omega_{prod,}$ f(x) = capacity in kt/a

x	f(x)
0	0
0,5	39642
5	32770859
8	56455650767

Table 7.2 Fixing the distillation cost at 50$/t to obtain the distillation cost line in function of the Ωprod, x= Ωprod, f(x) = capacity in kt/a

x	f(x)
1	2
5	93
10	1661
15	185159

Table 7.3 Fixing the distillation cost at 100$/t to obtain the distillation cost line in function of the Ωprod, x= Ωprod, f(x) = capacity in kt/a

x	f(x)
1	0
5	7
10	46
15	196
20	830
25	4814
30	92579

Table 7.4 Fixing the distillation cost at 150$/t to obtain the distillation cost line in function of the Ωprod, x= Ωprod, f(x) = capacity in kt/a

x	f(x)
1	0,1
5	1,9
10	9,9
15	30,9
20	81,9
25	208,6
30	553,6
35	1677,0
40	6844,4
45	61719,6

7.3 Appendix C – H_{vap} correction mean

0.5 GJ/t_{feed} is not the actual mean, but from the results it was found to be the best number for the results. The 0.5 was the usual value in the beginning of the research, at the end with all the compounds the mean was 0.4 GJ/t not considering Methanol or water. In the following table it can be seen that there is only a slight improvement by using the mean of 0.5 GJ/t_{feed}. Process 187 and 196 obtain worst results by using 0,4.

Process	Mean 0,4
163	0
184	0
187	-0,6
189	0
193	0
196	-0,4
199	0
201	0
203	0,6
207	0

Figure 7.1 Comparison for the Hvap means, showing the improvement obtained by using the 0,4 mean on the calculations, yellow representing a improvement under 0,5 GJ/t_{feed}.

Also it is clear that from this results using one of the two doesn't influence a lot the outcome, for the simplicity the value of 0.5 was chosen for the rest of the research.

7.4 Appendix D - Results for the reboiler vs total duty trend

In the article of J. P. Lange the assumption is made that the total duty represents double the firing duty. To verify this fact and compare it with his data the two following figures are shown.

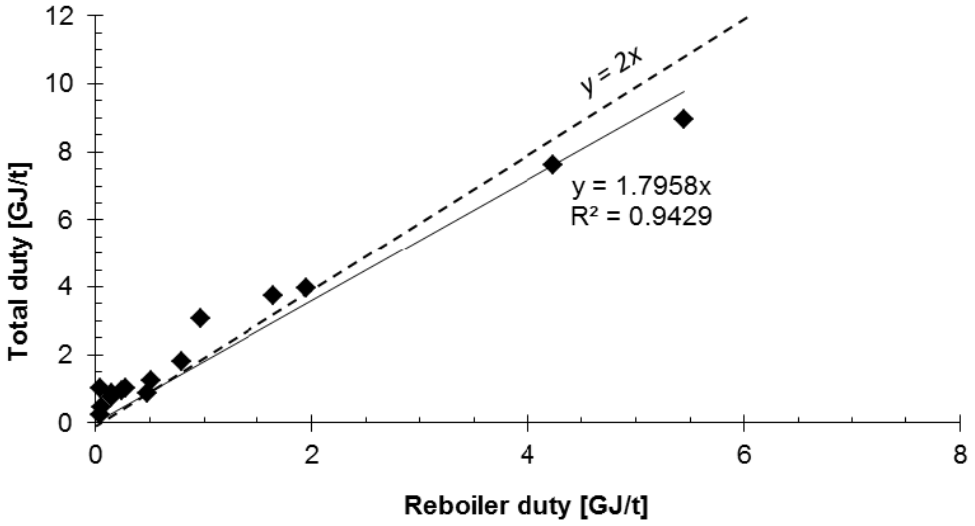

Figure 7.2 Reboiler total duty correlation to show the ratio of the reboiler and condenser from the article referred([6])

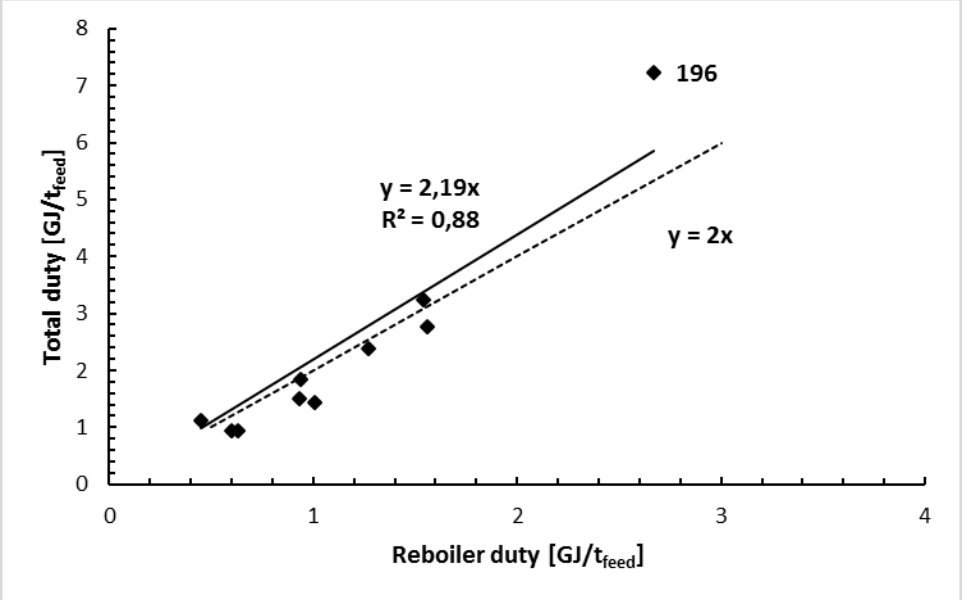

Figure 7.3 Total duty vs reboiler duty to check the correlation (research results)

In comparison to the results from the paper[16], the values approach the trend line of 2x on the upper side. During the research it was observed that a lot of times the first distillation column of the train this trend was not the case, but almost always for the second column this balance was reestablished, as observed below.

Table 7.5 Comparison of the condenser/reboiler duties along the separation train of process 187

	T-100	T-101	T-102	T-103
Reboiler (GJ/h)	107	64	43	111
Condenser (GJ/h)	31	99	50	104
Total (GJ/h)	138	163	93	214

The inlet feed stream for this case isn't in the optimal conditions, by entering at 15ºC and the distillate stream having at least 35ºC to separate the Propyleneoxide and lighters the reboiler has to supply more duty than the condenser. At the last column of the train the usual behavior is reestablished with the total duty being around 2x the reboiler duty.

The major Outlier, seen in figure 10, is process 196 here water is distilled at the top, the stream enters the column at already 123 ºC, 23 ºC over the boiling point of water. This explains the higher duty observed in the condenser in comparison to the reboiler.

7.5 Appendix E – Special cases: azeotropes

In the following pages the different azeotrope cases are analyzed for process 163 different lumping methods.

Table 7.6 Azeotropic information give by *Aspen Plus* for the water-benzene

	Water	Benzene
Mol %	43%	57%
Mass %	15%	85%
NBP (ºC)	57,25	

Table 7.7 Azeotropic information give by *Aspen Plus* for the water-ethylene

	Water	Ethylene
Mol %	71%	29%
Mass %	29%	71%
NBP ºC	79,33	

When the priority is given for the water – benzene azeotrope.

Table 7.8 Fraction lumping with priority for the water benzene azeotrope

Compound	Flow [ton/h]	Feed wt %	NBP [ºC]

Ethylene	3	1	-104
Water benzene	162	59	57,25
Water Ethylene	21	8	79,33
Ethylbenzene	75	28	136
Diethylbenzene	11	4	180
Total	273	100	

Table 7.9 Lumping for separation with priority for the water benzene azeotrope

Compounds	Feed wt % [x100]	NBP [ºC]	ΔT_{AB} [ºC]	Ω_d [100/ºC]
Water+Benzene+Ethylene	68	49	87	0,8
Ethylbenzene	28	136	44	0,6
Diethylbenzene	4	180		
Total	**100**			**1,4**

Table 7.10 Distillation resistance results using the variables for the azeotropic mixture (1^{st})

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,9	0,9	0,1
Total (GJ/t_{feed})	1,8	1,6	0,3

If priority is given to the other azeotropic mixture.

Table 7.11 Fraction lumping with priority for the water ethylene azeotrope

Compound	Flow [ton/h]	Feed wt %	NBP [ºC]
Water benzene	152	56	57,25
Benzene	9	3	79
Water Ethylene	25	9	79,33
Ethylbenzene	75	28	136
Diethylbenzene	11	4	180
Total	273	100	

Table 7.12 Lumping for separation with priority for the water ethylene azeotrope

Compounds	Feed wt % [x100]	NBP [ºC]	ΔT_{AB} [ºC]	Ω_d [100/ºC]
Water+Benzene+Ethylene	68	71	65	1,1
Ethylbenzene	28	136	44	0,6
Diethylbenzene	4	180		
Total	**100**			**1,7**

Table 7.13 Distillation resistance results using the variables for the azeotropic mixture (2nd)

Duty	Flow Sheet	Correlation	Absolute Deviation
Firing (GJ/t_{feed})	0,9	1,0	0,1
Total (GJ/t_{feed})	1,8	1,8	0,0

7.1 Appendix F – Duty estimation results

7.1.1 Distillation Section

All the results obtained for the different distillation sections are represented in the following table and compared to their respective *Unisim* estimation value.

Table 7.14 Results for the distillation resistance corrected for the Hvap in process 196

	163	184	187	189	193	196	199	201	203	207
Ω_d [100/ºC]	1,6	0,5	1,8	0,4	1,5	6,0	3,1	1,5	0,9	1,2
Reboiler (GJ/t_{feed})	0,9	0,6	1,3	0,6	0,4	2,7	1,5	1,0	1,6	0,9
Firing Ω_d(GJ/t_{feed})	0,9	0,3	1,0	0,2	0,8	3,4	1,8	0,8	0,5	0,7
Absolute Deviation	0,0	0,3	0,2	0,4	0,4	0,7	0,2	0,2	1,0	0,2
Total(GJ/t_{feed})	1,8	1,0	2,4	0,9	1,1	7,2	3,2	1,4	2,8	1,5
Total Ω_d(GJ/t_{feed})	1,8	0,6	2,0	0,4	1,6	6,6	3,5	1,6	1,0	1,4
Absolute Deviation	0,1	0,4	0,4	0,5	0,5	0,6	0,2	0,2	1,8	0,1

Individually represented duty values normalized per ton of product are shown in the following table.

Table 7.15 Comparison duty of the distillation sections with the *Unisim* normalized per ton of product

Process	Ω_{prod}	Reboiler (GJ/t_{prod})	Condenser (GJ/t_{prod})	Total *Unisim*	Total Estimated
196	35,3	20,1	18,7	42,5	38,8
187	11,3	6,5	6,0	14,9	12,5
199	10,1	5,8	5,4	10,4	11,1
163	5,7	3,2	3,0	6,5	6,3
207	5,4	3,1	2,9	6,5	6,0
184	3,0	1,7	1,6	5,3	3,3
193	1,9	1,1	1,0	1,4	2,0
203	1,6	0,9	0,8	4,8	1,7
201	1,5	0,8	0,8	1,4	1,6
189	0,4	0,2	0,2	0,9	0,4

7.1.2 Reaction Section (Heat exchangers + reactor)

Reaction section duty results per ton of product and per ton of feed for each process and represented also for each section contribution.

Table 7.16 Results for all the reaction section normalized per ton of product 1 part

Process	**184**		**187**		**189**	**193**		
	1	**2**	**1**	**2**	**1**	**1**	**2**	**3**
				Heat Exchanger				
***Unisim* (GJ/t_{prod})**	0,3	1,0	0,0	6,8	1,6	2,4	0,1	0,6
Estimated (GJ/t_{prod})	0,4	0,8	0,1	12,4	0,7	2,6	0,3	0,5
				Reactor				
***Unisim* (GJ/t_{prod})**	0,4	0,0	3,6	0,0	1,2	0,0	0,4	0,5
Estimated (GJ/t_{prod})	0,4	0,0	3,8	1,6	1,3	0,2	0,4	0,4
				Total				
***Unisim* (GJ/t_{prod})**	0,8	1,0	3,6	6,8	2,8	2,4	0,5	1,0
Estimated (GJ/t_{prod})	0,8	0,8	3,9	13,9	2,0	2,8	0,7	0,9
Absolute Deviation	**0,0**	**0,2**	**0,3**	**7,1**	**0,8**	**0,4**	**0,3**	**0,1**

Table 7.17 Results for all the reaction section normalized per ton of product 2nd part

196		**199**		**203**		**207**	
1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
			Heat Exchanger				
0,5	2,2	6,6	5,7	6,2	8,5	0,3	0,2
2,9	1,4	9,7	3,9	2,9	1,0	0,3	0,2
			Reactor				
0,0	0,0	5,4	0,0	2,7	0,3	1,2	1,0
0,2	0,5	5,5	0,3	2,4	0,5	1,4	1,2
			Total				
0,5	2,2	12,0	5,7	8,9	8,8	1,5	1,2
3,1	1,9	15,2	4,2	5,3	1,5	1,7	1,4
2,6	**0,3**	**3,2**	**1,5**	**3,6**	**7,3**	**0,3**	**0,2**

Table 7.18 Results for all the reaction section normalized per ton of feed 1 part

Process	184		187		189	193		
	1	2	1	2	1	1	2	3
				Heat Exchanger				
Unisim **(GJ/t_{feed})**	0,2	0,1	0,0	0,1	1,4	0,4	0,1	0,4
Estimated (GJ/t_{feed})	0,2	0,0	0,0	0,1	0,6	0,4	0,3	0,4
				Reactor				
Unisim **(GJ/t_{feed})**	0,2	0,0	0,5	0,0	1,0	0,0	0,4	0,4
Estimated (GJ/t_{feed})	0,2	0,0	0,6	0,01	1,1	0,0	0,4	0,3
				Total				
Unisim **(GJ/t_{feed})**	0,4	0,1	0,5	0,1	2,4	0,4	0,5	0,8
Estimated (GJ/t_{feed})	0,4	0,0	0,6	0,1	1,8	0,5	0,7	0,7
Absolute Deviation	**0,0**	**0,0**	**0,0**	**0,1**	**0,7**	**0,1**	**0,2**	**0,1**

Table 7.19 Results for all the reaction section normalized per ton of feed 2nd part

196		199		203		207	
1	2	1	2	1	2	1	2
			Heat Exchanger				
0,0	0,4	0,5	0,7	0,9	3,6	0,2	0,1
0,1	0,2	0,7	0,5	0,4	0,4	0,2	0,2
			Reactor				
0,0	0,0	0,4	0,0	0,4	0,1	0,7	0,8
0,0	0,1	0,4	0,0	0,4	0,2	0,8	0,9
			Total				
0,0	0,4	0,9	0,7	1,3	3,8	0,8	0,9
0,1	0,3	1,1	0,5	0,8	0,7	1,0	1,1
0,1	**0,1**	**0,2**	**0,2**	**0,5**	**3,1**	**0,1**	**0,2**

7.1.3 Reaction Section (Heat Exchangers)

Duties for the heat exchangers, comparing the results for the different coefficient used in the equation.

Table 7.20 Absolute deviation in function of the factor used for the heat exchangers part 1

Process	184-1	184 - 2	187 - 1	187 - 2	189 - 1	193 - 1
Unisim **(GJ/t_{prod})**	0,3	1,0	0,0	6,8	1,6	2,4
With Heat Integration	0,3	0,8	0,1	12,4	0,7	2,6
Dedicated Heater cooler	0,5	1,2	0,2	18,5	1,1	3,9
No Heat Integration	0,7	1,5	0,3	24,7	1,5	5,2

Table 7.21 Absolute deviation in function of the factor used for the heat exchangers part 2

193 - 2	193 - 3	196 - 1	196 - 2	199 - 1	199 - 2	203 - 1	203 - 2	207 - 1	207 - 2
0,1	0,6	0,5	2,2	6,6	5,7	6,2	8,5	0,3	0,2
0,3	0,5	2,9	1,4	9,7	3,9	2,9	1,0	0,3	0,2
0,5	0,7	4,3	2,1	14,5	5,8	4,4	1,5	0,5	0,4
0,6	1,0	5,8	2,8	19,4	7,7	5,8	2,0	0,7	0,5

Figure representing only the heat exchange duties compared to their respective Unisim value organized by increasing process number.

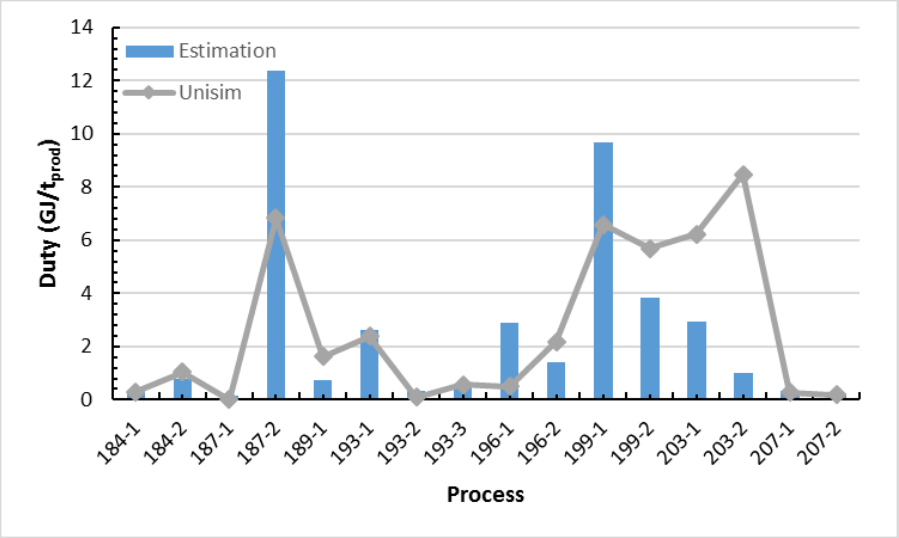

Figure 7.4 Estimation vs correlation for the heat exchangers individually for each reaction section organized by increasing process number.

Clear to see in the figure that large deviations exist. These are present mostly in process 203 and 199 which have a lot of aqueous compounds present, same as in process 187. For this reason the assumptions can't always be fulfilled and deviations occur.

The following table gives a good overlook possible reasons for the deviations in the heat exchanger estimations.

Table 7.22 Deviation explanation heat exchanger estimation reaction section, until 0,5 GJ/t_{prod} deviation is seen as acceptable

Process	Deviation (GJ/t_{prod})	Reason
184-1	0,0	Acceptable deviation
184-2	0,3	Acceptable deviation
187-1	-0,1	Acceptable deviation
187-2	-5,5	* Partial (61%) condensation of Water and Methanol
189-1	0,9	Acceptable deviation
193-1	-0,2	Acceptable deviation
193-2	-0,2	Acceptable deviation
193-3	0,1	Acceptable deviation
196-1	-2,4	* The inlet feed stream comes in at 80ºC and is heated to 83ºC and not cooled afterwards
196-2	0,8	Acceptable deviation
199-1	-3,1	* Vaporization of MeOH feed
199-2	1,8	*Partial condensation 29%
203-1	3,3	*(12%) Partial condensation of Water and Methanol
203-2	7,4	* Liquid vaporization including MeOH and Water
207-1	-0,1	Acceptable deviation
207-2	-0,1	Acceptable deviation

7.1.4 Reaction Section (Reactor)

Same graph as seen for the heat exchanger part, representing the individual comparison in between the Unisim values and the estimations. Good to see here the accuracy of the estimation.

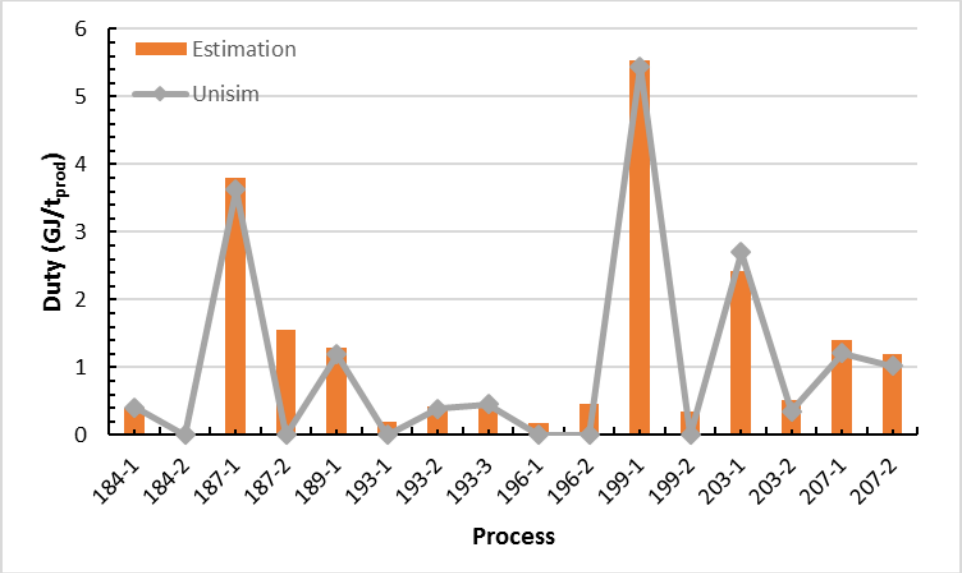

Figure 7.5 Estimation vs correlation for the reactors for each reaction section

7.2Appendix G - CapEx estimations

7.2.1 CEPCI

The following table illustrates the different CEPCI Values used for the research

Table 7.23 CEPCI Values for the different process [10]

	CEPCI						
Process	**-**	**163**	**184**	**187**	**193**	**199**	**207**
Year	2003	2006	2012	2012	2014	2015	2015
CEPCI	402	499,6	584,6	584,6	576,1	573,1	573,1

7.2.2 Distillation Section

Comparing the different ISBL conversion factors it seems that actually factor 6.3 should be the one to use although it includes also OSBL costs.

Table 7.24 ISBL values using different factors [2]

Process	163	184	187	199	207
Typical factor (3,3)	19	2	18	6	1
Hand factor (4-Distillation columns, 3,5 Heat Exchanger)	21	2	21	7	2
Lang (4,74)	27	2	26	9	2
Lang (All Fixed costs -6.3)	36	3	35	12	3

Table 7.25 Feed x distillation resistance CapEx correlation table

Process	163	184	187	199	207
Resistance	1,6	0,5	2,2	3,1	1,2
Feed kt/a	2183	191	2043	618	96
Rd*Flow	3482	103	4494	1940	119
Heat Exchanger (M$) - 2003	4,1	0,1	1,6	0,9	0,2
Distillation Column (M$) - 2003	1,7	0,4	4,0	1,1	0,3
Typical Factor	19	2	18	6	1
Hand factor	21	2	21	7	2
Lang	27	2	26	9	2
Lang (All Fixed costs -6.3)	36	3	35	12	3

Table 7.26 Duty (MW) CapEx correlation for the distillation section using Lang factor 4.74

Process	163	184	187	199	207
Resistance	1,6	0,5	2,2	3,1	1,2
Lang	27	2	26	9	2
Total Heat (MW *Unisim*)	139	6	169	69	5

7.2.3 Reaction Section

Table 7.27 CapEx results for the reaction section converted to M$ 2003

Process	187		189		193		196		199	
	1	2	1	1	2	3	1	2	1	2
CapEx (M$ 2003) Reactor	5,93	0,05	3,4	0,06	0,12	0,05	0,46	1,55	1,69	0,57
CapEx (M$ 2003) HE	0	0,08	0,1	0,27	0,02	0,04	0,03	0,04	0,82	1,11
Section (M$ 2003)	5,93	0,13	3,5	0,33	0,14	0,09	0,49	1,59	2,51	1,68
Section (M$ 2003)-Lang	**27,9**	**0,6**	**16,5**	**1,5**	**0,7**	**0,4**	**2,3**	**7,5**	**11,8**	**7,9**
Duty *Unisim* (MW)	37	2	94	54	11	19	0	2	34	40
Duty estimated (MW)	41	3	67	63	17	18	3	2	43	29

A suspicion was that the deviations could end up being more associated to the sections were the majority of the duty was from the heat exchangers, as a matter of fact the two process have 100% of their energy needs from the heat exchangers seen that they have an adiabatic reactor present.

Meaning with this that the equation proposed for the correlation may estimate more accurately reactors than heat exchangers. Seen that a reactor is more expensive to build with a heat exchanger than a simple heat exchanger.

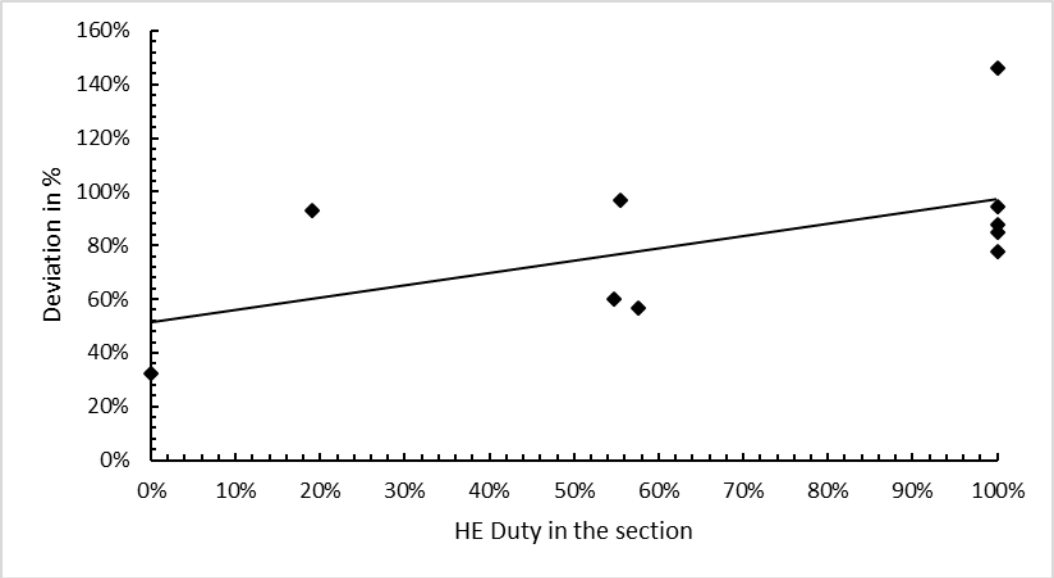

Figure 7.6 Correlation Heat exchanger duty in function of deviation (*Unisim* data subtracting the estimation dividing through the *unisim* value shown in percentage) in function of the HE duty in relation to the to the total duty of the section (Reactor + HE)

From this graph it seems to exist some kind of correlation, but no confirmation can be made as for now, beside to flag the situation.

7.2.4 Correlation of Payback ratio to high duty

A comparison was made out of interest with the payback time of the process in order to give an indication of profitability.

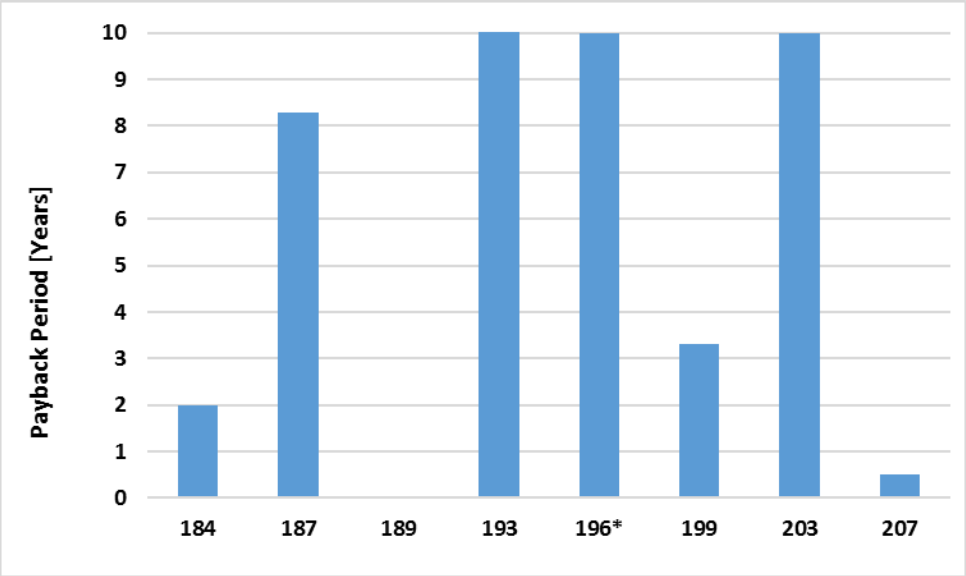

Figure 7.7 Payback ratio analysis

Process 193, 196 and 203 are not feasible. Process 189 has no calculation concerning Payback time. After looking at this graph more clear indication of the margin that can be given for the duty requirements should come from the gross margin as here is the biggest money maker or breaker.